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BAND SPECTRUM AND STRUCTURE OF THE BCl MOLECULE[1]

BY G. HERZBERG[2] AND W. HUSHLEY[3]

Abstract

The $^1\Pi - {}^1\Sigma^+$ system of the BCl molecule has been photographed in the sixth order of a 20 ft. grating. The previous interpretation of the vibrational structure by Miescher (5) is slightly modified. The new formula for the Q heads of the $B^{11}Cl^{35}$ molecule is

$$\nu = 36750.92 + 849.04(v'+\tfrac{1}{2}) - 11.37(v'+\tfrac{1}{2})^2 - 0.100(v'+\tfrac{1}{2})^3$$
$$- 0.0271 \ (v'+\tfrac{1}{2})^4 - [839.12(v''+\tfrac{1}{2}) - 5.11(v''+\tfrac{1}{2})^2]$$

The fine structure of a number of bands has been measured and analysed, leading to the following accurate values for the rotational constants: $B'_e = 0.7054$ cm.$^{-1}$, $\alpha'_e = 0.00820$ cm.$^{-1}$, $B''_e = 0.6838$ cm.$^{-1}$, $\alpha''_e = 0.00646$ cm.$^{-1}$. The internuclear distance in the ground state is $r''_e = 1.716.10^{-8}$ cm. The molecular constants of BCl are compared with those of the iso-electronic molecules CS, PN, and SiO as well as with those of BBr, BCl$_3$, and BBr$_3$.

A. Introduction

Jevons (4) in 1924 discovered a band system of BCl in the region 2600 to 2900Å in a discharge through boron trichloride vapour. The vibrational structure of this system was analysed in 1935 by Miescher (5). While investigating the band spectra of the molecules B_2 and BN we found it possible to obtain the BCl spectrum with sufficiently high dispersion to make possible a rotational analysis. In the course of the investigation it turned out that Miescher's interpretation of the vibrational structure had to be changed somewhat. An accurate knowledge of the vibrational and rotational constants of BCl obtained here should be of interest particularly for a comparison with other diatomic molecules and with certain polyatomic molecules.

B. Experimental

The BCl spectrum was excited in an ordinary uncondensed discharge through helium to which a small amount of boron trichloride vapour had been added. Such a discharge is preferable to one through boron trichloride vapour alone, since, in the latter, higher rotational levels are excited which give rise to a much greater complexity of the spectrum.

The spectrum was taken in the sixth order of the Saskatoon 20 ft. grating. The exposure times were 3 to 15 hr. Figs. 1 and 2 give enlargements of the spectra obtained. The band lines were measured against iron lines of the fifth and sixth orders by means of a Gaertner comparator.

C. Vibrational Analysis

The ultra-violet BCl bands represent a band system with well developed sequences (see Fig. 1). The vibrational analysis would therefore be very simple if it were not for the facts that four isotopic species, $B^{11}Cl^{35}$, $B^{10}Cl^{35}$, $B^{11}Cl^{37}$, $B^{10}Cl^{37}$ exist, whose spectra overlap, that the bands are not all shaded in the same direction, and that in general each one has two heads. At first sight the analysis given by Miescher (5) would appear to be correct. But there are two points in the vibrational structure that cannot be explained on its basis: (1) The two bands 37580.39 and 37552.45 cm.$^{-1}$ are assigned by Miescher as 1–0 bands of $B^{10}Cl^{35}$ and $B^{11}Cl^{35}$ respectively in spite of the fact that their intensity ratio 8 : 7 (as given by Miescher and confirmed by our plates, Fig. 1) disagrees radically with the abundance ratio 1 : 4 (approximately) of the two isotopic species. Very artificial assumptions would be necessary to explain this unless one assumes that the two bands are the 1–0 and 2–1 bands of $B^{11}Cl^{35}$ and increases the numbering of the succeeding bands correspondingly. Indeed, on our plates two further weaker bands appear at 37610.41 and 37605.17 (see Fig. 1), which are naturally explained as 1–0 bands of $B^{10}Cl^{35}$ and $B^{10}Cl^{37}$. These bands have not been found by Miescher apparently because they were hidden by the rotational structure of the preceding bands which extend in his source much further than in ours. (2) In the $\Delta v = 0$ sequence the strong band head 36751.10 has not been assigned by Miescher although it is given by him. The only possible explanation on the basis of Miescher's analysis is that it is the $B^{10}Cl^{35}$ isotopic band belonging to the main band 36754.22 which Miescher considers as 0–0. However, the isotope shift would then be far too large (4.1 cm.$^{-1}$ against a value of 0.33 cm.$^{-1}$ calculated from Miescher's formula). The only reasonable explanation seems to be that the band 36751.10 is the 1–1 of $B^{11}Cl^{35}$, and that the 0–0 and 1–1 bands of $B^{10}Cl^{35}$ are not separated from the corresponding $B^{11}Cl^{35}$ bands. On this assumption the numbering of the succeeding bands in this sequence has of course to be raised by one unit. In fact, a reasonable variation in the $\Delta G'$ and $\Delta G''$ values can be obtained only by raising the numbering in all sequences simultaneously.

Table I gives the Deslandres table for the Q heads of $B^{11}Cl^{35}$ and $B^{10}Cl^{35}$ with the new assignment. Wherever available our new wave numbers obtained under high dispersion are given while for the bands that we could not measure Miescher's values are used. The former are given with one more decimal place.

PLATE I

FIG 1a.

FIG. 1b.

PLATE II

FIG. 2.

TABLE I

DESLANDRES TABLE OF THE ULTRA-VIOLET BCl BANDS

The upper figure for a given v' and v'' is the wave number of the Q head of $B^{11}Cl^{35}$, the lower figure that of the Q head of $B^{10}Cl^{35}$. Overlapped bands are in square brackets. The figures in parentheses are the deviations from Formulae (1) and (2) respectively.

v'' \ v'	0	1	2	3	4	5	6	7	8
0	36754.22(−.08) [36754.2](−.2)	[35925.2](−.2) 35895.0(−.1)							
1	37580.39(+.25) 37610.41(+.45)	36751.10(−.14) 36750.10(−.56)	35931.9(−.7)						
2	38381.5(−.1) 38439.0(−.2)	37552.45(−.21) [37580.4](+.5)	36733.92(−.08)	[35925.2](−.3)					
3			37508.70(−.38) 37531.71(−.55)	36700.48(−.14) 36694.81(−.16)	35903.3(+.9) 35870.4(+1.7)				
4				37446.00(−.85) 37462.81(−1.33)	36648.44(−.17) 36637.63(+.22)	35860.4(−.2) 35823.0(+.4)	35082.8(0.0)		
5				38158.7(−2.3)	37362.4(−.4) 37370.0(−1.8)	36574.54(−.21) 36556.33(−.24)	35796.5(−.5) 35753.8(+1.5)	35529.3(−.1)	
6					38041.1(+.1)	37253.4(+.4)	36475.31(+12)	35707.7(+.1)	
7						37890.8(0.0)		36345.0(−.4)	
8									36180.0(−.3)

TABLE II

Wave numbers of band lines

J	0-0 Band			1-0 Band			3-3 Band		4-3 Band	
	R(J)	Q(J)	P(J)	R(J)	Q(J)	P(J)	R(J)	P(J)	R(J)	P(J)
6		36754.94	36747.13				36710.16	36692.69		37438.19
7	36766.44	55.24	45.93			37571.29	11.64	91.44	37456.61	36.67
8	68.12	55.56	44.77	37693.54		70.10	13.18	90.28	57.81	35.40
9	69.89	55.94	43.56	95.05		68.95	14.77	89.15	59.12	34.07
10	71.76	56.41	42.42	96.80		67.77	16.11	87.96	60.38	32.62
11	73.63	56.83	41.45	98.39		66.69	17.65	86.89	61.60	31.35
12	75.53	57.32	40.51	37700.08		65.53	19.27	85.75	62.81	29.94
13	77.53	57.87	39.66	01.76	37582.41	64.45	20.59	84.75	64.11	28.61
14	79.45	58.46	38.87	03.52	82.71	63.36		83.66	65.37	27.22
15	81.52	59.13	38.07	05.17	83.04	62.34		82.55	66.63	25.81
16	83.59	59.82	37.22	06.89	83.41	61.36	25.67	81.48	67.79	24.42
17	85.75	60.49	36.71	08.61	83.79	60.20	27.25	80.46	68.97	23.00
18	87.88	61.29	36.05	10.41	84.21	59.29	29.04	79.51	70.28	21.63
19	90.03	62.06	35.44	12.21	84.65	58.40	30.89	78.52	71.48	20.17
20	92.29	62.97	34.91	14.05	85.09	57.38	32.50	77.55	72.64	18.81
21	94.59	63.76	34.42	15.93	85.54	56.56	34.42	76.62	73.84	17.43
22	96.90	64.66	33.89	17.74	86.05	55.67	36.05	75.73	75.02	15.91
23	99.25	65.65	33.45	19.64	86.55	54.79	37.62	74.80	76.18	14.50
24	36801.65	66.66	33.05	21.54	87.07	53.94	39.66	73.92	77.30	13.04
25	04.09	67.65	32.77	23.48	87.60	53.15	41.45	73.10	78.39	11.61
26	06.57	68.75	32.50	25.43	88.19	52.45		72.19	79.43	10.07
27	09.08	69.89	32.24	27.39	88.85	51.65		71.34	80.59	08.62
28	11.64	71.12		29.37	89.39	50.81		70.47	81.78	07.08
29	14.24	72.35		31.30	90.00	50.03		69.77		05.62
30	16.87	73.63			90.57	49.32		68.93		
31	19.55	74.90		35.38	91.33	48.65		68.23		
32	22.39	76.24		37.41	92.05	47.92		67.44		
33	25.02	77.53		39.52	92.68	47.34		66.77		
34	27.82	79.08		41.61	93.54	46.78		66.01		
35	30.65	80.47		43.70	94.22	46.07		65.29		
36	33.46	81.97		45.81				64.59		
37	36.40	83.59		48.05				63.91		
38	39.36	85.07		50.11						
39	42.35	86.67		52.18						
40	45.34	88.32								
41	48.37	90.03								
42	51.51	91.79								
43	54.62	93.51								
44	57.77	95.26								
45	61.00	97.15								
46	64.22	99.25								
47		36801.02								
48		03.01								

The B^{11}Cl^{35} Q heads, which are essentially the zero lines, can be represented by the formula

(1) $\nu(\text{B}^{11}\text{Cl}^{35}) = 36750.92 + [849.04(v'+\frac{1}{2}) - 11.37(v'+\frac{1}{2})^2 - 0.100(v'+\frac{1}{2})^3$
$- 0.0271(v'+\frac{1}{2})^4] - [839.12(v''+\frac{1}{2}) - 5.11(v''+\frac{1}{2})^2].$

The deviations (observed minus calculated) from this formula are given in parentheses after each wave number in Table I. On the basis of the above formula also a few band heads unidentified by Miescher could be assigned.

According to the elementary theory of the isotope effect [see Herzberg (3)] the formula that should hold for the other isotopic species can be easily

TABLE II—*concluded*

WAVE NUMBERS OF BAND LINES—*concluded*

J	4–4 Band		5–5 Band		6–6 Band		
	R(J)	P(J)	R(J)	P(J)	R(J)	Q(J)	P(J)
2			36578.51		36479.03		
3			79.75		80.21		
4			81.02		81.39		
5			82.26	36568.17	82.56		
6			83.54	66.74	83.67		
7			84.80	65.47	84.79		
8	36660.49		86.06	64.12	85.85		
9	61.85	36636.88	87.30	62.81	86.89		36462.97
10	63.19	35.65	88.50	61.46	87.94		61.51
11	64.59	34.40	89.72	60.08	88.92	36473.84	60.02
12	66.01	33.22	90.93	58.74	89.94	73.54	58.42
13	67.44	32.01	92.17	57.34	90.90	73.26	56.91
14	68.93	30.77	93.34	56.02	91.83	72.92	55.31
15	70.47	29.57	94.53	54.63	92.70	72.55	53.66
16		28.39	95.72	53.23	93.58	72.14	52.18
17	73.10	27.20	96.86	51.85	94.44	71.77	50.42
18	74.80	25.97	98.02	50.43	95.26	71.35	48.76
19	76.10	24.74	99.20	49.02	96.03	70.89	47.05
20	77.55	23.73	36600.34	47.63	96.80	70.43	45.28
21	78.94	22.54	01.46	46.20	97.46	69.94	43.54
22	80.46	21.43	02.61	44.77	98.23	69.34	41.76
23	81.86	20.27	03.68	43.31	98.93	68.76	39.93
24	83.45	19.16	04.78	41.87	99.55	68.19	38.09
25	84.75	18.04	05.85	40.39	36500.05	67.53	36.22
26	86.29	16.85	06.87	38.99	00.73	66.84	34.30
27	87.78	15.81	07.99	37.45	01.22	66.16	32.40
28	89.15	14.62	09.07	35.98	01.70	65.41	30.42
29	90.70	13.51	10.15	34.43	02.17	64.66	28.46
30	92.11	12.40	11.28	32.94	02.57	63.84	26.39
31	93.62	11.28	11.99	31.42	02.96	62.97	24.35
32		10.15	12.95	29.90	03.33	62.11	22.21
33		09.07	13.95	28.36		61.17	20.08
34			14.85	26.68		60.25	17.91
35			15.81	25.14		59.30	15.68
36				23.48		58.42	13.43
37				21.92			11.10
38				20.27			08.83
39				18.57			06.41
40				16.89			04.02
41				15.11			

obtained from Equation (1). For $B^{10}Cl^{35}$ we found using $\rho = \sqrt{\dfrac{\mu}{\mu^i}} = 1.03715$

(μ and μ^i are the reduced masses of $B^{11}Cl^{35}$ and $B^{10}Cl^{35}$ respectively).

(2) $\nu(B^{10}Cl^{35}) = 36750.92 + [880.58(v' + \frac{1}{2}) - 12.23(v' + \frac{1}{2})^2 - 0.1116(v' + \frac{1}{2})^3 - 0.0313(v' + \frac{1}{2})^4] - [870.29(v'' + \frac{1}{2}) - 5.50(v'' + \frac{1}{2})^2].$

The deviations of the observed $B^{10}Cl^{35}$ bands from this formula are also given in parentheses in Table I. It is seen that the agreement is very satisfactory. This is another confirmation of the new vibrational analysis since Miescher in his analysis found deviations between observed and calculated isotope shifts up to 6 cm.$^{-1}$.

A further important confirmation of the new vibrational assignment comes from the rotational analysis (see below).

It should be noted that the strong head at 36731.60 cm.$^{-1}$ which was considered as Q head of the 1–1 band by Miescher is actually the P head of the 0–0 band of $B^{11}Cl^{35}$. This is shown by the fact that it occurs at exactly the place where it is expected from the analysis of the rotational structure (see below) and that, if considered as 2–2 band in our numbering, it would give a deviation of 2.4 cm.$^{-1}$ from the formula, which is much greater than the accuracy of the measurements. The actual 2–2 band can just be recognized at 36733.92 cm.$^{-1}$ under the stronger P head of the 0–0 band. The head at 36730.25 is obviously the corresponding P head of the 0–0 band of $B^{10}Cl^{35}$, which no longer coincides with that of $B^{11}Cl^{35}$ on account of the rotational isotope shift. Similarly, the heads at 36724.98 and 36722.12 cm.$^{-1}$, which were considered as P heads of the 0–0 band by Miescher, must be interpreted as P heads of the 1–1 band of $B^{11}Cl^{35}$ and $B^{10}Cl^{35}$ respectively.

D. Rotational Analysis

As an illustration Fig. 2 gives a greatly enlarged reproduction of the fine structure of the 6–6 band. In spite of the slight overlapping by the isotopic bands the three branches P, Q, and R can be easily recognized; this confirms Miescher's conclusion that the band system represents a $^1\Pi{-}^1\Sigma$ transition. The numbering in the branches of the 6–6 band was obtained by systematic trial until the relation $R(J)-Q(J) = Q(J+1) - P(J+1)$ was fulfilled for all J values. This numbering also agrees with that obtained directly from the spectrogram for the R branch if it is assumed that the head of the Q branch is at ν_0 (see Fig. 2). In a similar way the 0–0 and 1–0 bands were analysed. For them the correctness of the numbering is further confirmed by the exact agreement of the Δ_2F'' values which at the same time confirms the vibrational analysis. For the other bands measured, the Q branch was not or not as well resolved. But for them the numbering could be obtained from the position of the Q head or the agreement of combination differences in two bands of the same v' or the same v''.

Table II gives the wave numbers of the band lines in all the analysed bands. In order to save space we refrain from giving all the combination differences but illustrate only in Table III the kind of agreement obtained by the values of $\Delta_2F''(J) = R(J-1) - P(J+1)$ of the 0–0 and 1–0 bands as far as they can be formed for both bands. The excellent agreement of the two columns supplies the final proof for our new vibrational numbering. According to Miescher's analysis the two bands are the 0–0 band of $B^{11}Cl^{35}$ and the 1–0 band of $B^{10}Cl^{35}$ and therefore the Δ_2F'' should be quite different.

From the combination differences the rotational constants B_v and D_v were obtained in the usual way [see Herzberg (3)]. As far as possible Δ_2F values were used but in those cases in which the P or the R branch was not measurable Δ_1F values had to be used. The latter procedure is open to objection only

TABLE III

COMBINATION DIFFERENCES $\Delta_2 F''(J)$ FOR THE 0–0 AND 1–0 BANDS

J	0–0 Band	1–0 Band	J	0–0 Band	1–0 Band
9	25.70	25.77	18	50.31	50.21
10	28.44	28.36	19	52.97	53.03
11	31.25	31.27	20	55.61	55.65
12	33.97	33.94	21	58.40	58.38
13	36.66	36.72	22	61.14	61.14
14	39.46	39.42	23	63.85	63.80
15	42.23	42.16	24	66.48	66.49
16	44.81	44.97	25	69.15	69.09
17	47.54	47.60	26	71.85	71.83

when there is an appreciable Λ-type doubling in the $^1\Pi$ state. Actually for the bands in which all three branches could be measured no combination defect between $R(J) - Q(J)$ and $Q(J+1) - P(J+1)$, which would indicate a Λ-type doubling, was found. Also an independent determination of B_0'' from the $\Delta_2 F''$ values of the 1–0 band and from the $\Delta_1 F''$ values of the 0–0 band gave exact agreement.

TABLE IV

ROTATIONAL CONSTANTS OF $B^{11}Cl^{35}$

v	Upper state, $^1\Pi$		Lower state, $^1\Sigma^+$	
	B_v', cm.$^{-1}$	D_v', cm.$^{-1}$	B_v'', cm.$^{-1}$	D_v'', cm.$^{-1}$
0	0.7013	$1.80 \cdot 10^{-6}$	0.6806	$1.75 \cdot 10^{-6}$
1	0.6919	$1.92 \cdot 10^{-6}$		
2				
3	0.6704	$(2.46 \cdot 10^{-6})^*$	0.6612	$1.92 \cdot 10^{-6}$
4	0.6586	$2.70 \cdot 10^{-6}$	0.6549	$2.15 \cdot 10^{-6}$
5	0.6454	$3.05 \cdot 10^{-6}$	0.6483	$2.10 \cdot 10^{-6}$
6	0.6308	$3.45 \cdot 10^{-6}$	0.6419	$2.19 \cdot 10^{-6}$

*This value was obtained by interpolation between the other D_v' values.

The resulting values of B_v and D_v for the upper and lower states are listed in Table IV. The B_v values are also plotted against v in Fig. 3. It is seen that B_v'' is very closely a linear function of v'', while B_v' is decidedly curved. The values of B_e, α_e, γ_e in

$$(3) \qquad B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2$$

are given in Table V below.

The intersection of the B_v curves of the upper and lower states (Fig. 3) accounts for the fact that the direction of shading changes from violet to red in each sequence of the BCl bands. As previously noted by Miescher, for the bands nearest to the reversal of the shading, a reversal even within the band takes place, that is, one branch may have two heads or there may be a head in both the P and R branch. Fig. 1b shows clearly two opposing

heads in the Q branch of the 4–4 band of $B^{10}Cl^{35}$ and, not quite so clearly, for the corresponding band of $B^{11}Cl^{35}$. This effect is due to the term $DJ^2(J+1)^2$ in the energy formula [see Herzberg (3)]. In Fig. 4, $\Delta_1 F'$ and $\Delta_1 F''$
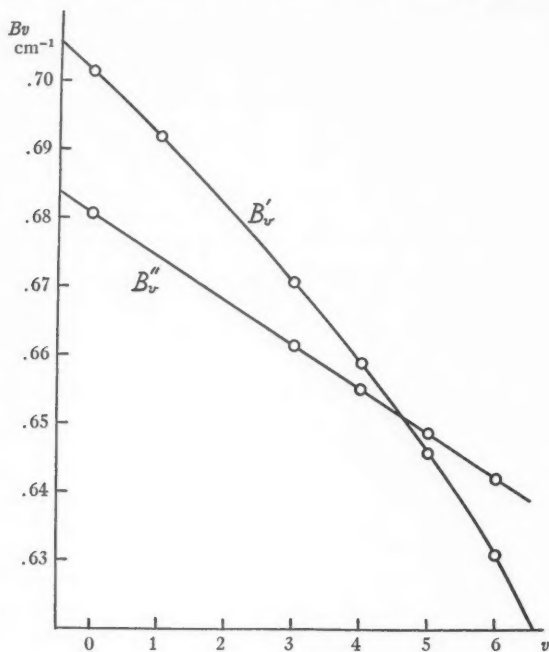

FIG. 3

TABLE V

MOLECULAR CONSTANTS OF $B^{11}Cl^{35}$

	Upper state, $^1\Pi$	Lower state, $^1\Sigma^+$
B_e, cm.$^{-1}$	0.7054	0.6838
B_0, cm.$^{-1}$	0.7012	0.6806
α_e, cm.$^{-1}$	0.00820	0.00646
γ_e, cm.$^{-1}$	0.00050	
D_e, cm.$^{-1}$	$1.60 \cdot 10^{-6}$	$1.72 \cdot 10^{-6}$
β_e, cm.$^{-1}$	$0.27 \cdot 10^{-6}$	$0.07 \cdot 10^{-6}$
r_0, cm.	$1.694 \cdot 10^{-8}$	$1.720 \cdot 10^{-8}$
r_e, cm.	$1.689 \cdot 10^{-8}$	$1.716 \cdot 10^{-8}$
I_e, gm.-cm.^{2}	$39.68 \cdot 10^{-40}$	$40.94 \cdot 10^{-40}$
ω_e, cm.$^{-1}$	849.04	839.12
$\omega_e x_e$, cm.$^{-1}$	11.37	5.11
$\omega_e y_e$, cm.$^{-1}$	-0.100	
$\omega_e z_e$, cm.$^{-1}$	-0.0271	
ν_e, cm.$^{-1}$	36750.92	

are plotted for the 4–4 band of $B^{11}Cl^{35}$ after subtracting $1.26(J+1)$. Where these two curves intersect, a head must occur since for those J values an increase of J does not change the position of the Q lines (since the change of energy is the same in the upper and lower state). It is seen that in addition to the ordinary Q head corresponding to $J = -1$ a second head is to be expected for $J=57$ because of the different curvature of the $\Delta_1 F$ curves (that is, different D values). Substituting into the formula for the Q branch, the wave number of the second head is predicted to be at 36654.66 cm.$^{-1}$ while the (not very accurate) observed value is 36654.3 cm.$^{-1}$.
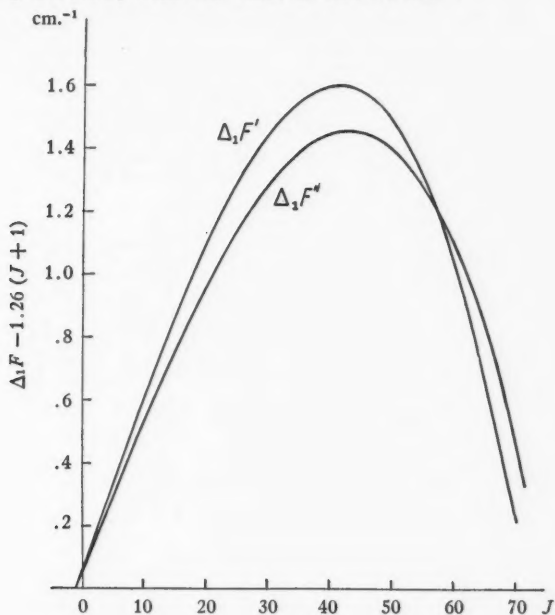
FIG. 4

It is clear from Fig. 4 that such an additional head can occur only when B' and B'' are very nearly equal (as for bands near the point of reversal of shading in a sequence) and when in addition D' is rather different from D'' and $D'-D''$ has the same sign as $B'-B''$.

E. Molecular Constants and Comparisons with Other Molecules

In Table V are listed the rotational as well as the vibrational constants of the $B^{11}Cl^{35}$ molecule that follow from the above analysis. The values for the internuclear distances and moments of inertia are based on the atomic constants used by Herzberg (3). $^1\Pi-^1\Sigma^+$ band systems very similar to the one investigated here for BCl have been observed to be the strongest transitions of the isoelectronic molecules CS, PN, and SiO. Since in the case of PN

TABLE VI

MOLECULAR CONSTANTS OF MOLECULES WITH 22 ELECTRONS ($^1\Pi$–$^1\Sigma^+$ TRANSITIONS)

Molecule	BCl	CS	PN	SiO
$r_e''(10^{-8}$ cm.$)$	1.716	1.536	1.491	1.510
$r_e'(10^{-8}$ cm.$)$	1.689	1.563	1.547	1.621
ω_e''(cm.$^{-1}$)	839.12	1285.1	1337.24	1242.03
ω_e'(cm.$^{-1}$)	849.04	1072.3	1103.09	851.51
ν_e(cm.$^{-1}$)	36750.92	38912.15	39805.66	42835.3
Reference	This paper	(1)	(2)	(7)

and SiO these $^1\Pi$–$^1\Sigma^+$ transitions have also been observed in absorption it may be concluded that for all four molecules the lower $^1\Sigma^+$ state is the ground state. Thus the data in the last column of Table V refer to the ground state of $B^{11}Cl^{35}$.

It is interesting to compare the molecular constants of the four isoelectronic molecules BCl, CS, PN, and SiO in the upper and lower states of their $^1\Pi$–$^1\Sigma^+$ transitions. Table VI gives the necessary data. As is to be expected the r_e values in both upper and lower states have a minimum, the ω_e values a maximum value for PN. However, it is rather unexpected that the value of the excitation energy ν_e increases from BCl to SiO (that is, with increasing atomic number of the lighter atom). Unfortunately, data for the next molecule in this series AlF are not available. But they could be predicted roughly on the basis of Table VI: the r_e and ω_e values should be similar to those of BCl, while the electronic excitation is probably even higher than that of SiO.* Relations very similar to those for BCl, CS, PN, SiO exist for the molecules BBr, CSe, AsN, and GeO.

Another interesting comparison can be made between the diatomic molecules BCl and BBr, on the one hand, and the four-atomic molecules BCl_3 and BBr_3, on the other. Table VII gives the boron-halogen internuclear distances r_0 and force constants k for these molecules. The r_0 values for the trihalides are electron diffraction values [taken from Pauling (6)], which have a much smaller accuracy than the spectroscopic values for the diatomic molecules. But within this accuracy (± 0.02) the boron-halogen distance is the same in the diatomic radical and the saturated polyatomic molecule. The force constants for the trihalides are those given by Wu (8) as obtained from the observed fundamental vibrations of these molecules. In order to give comparable values for the diatomic radicals their force constants have been evaluated from the $\Delta G_{\frac{1}{2}}''$ values not from ω_e or ω_0. Again the values agree

* *Note added in proof: In stating that no data for AlF are available, we overlooked, unfortunately, a paper by G. D. Rochester (Phys. Rev. 56 : 305-307. 1939) in which the absorption spectrum of AlF has been studied. The constants ω_e'', ω_e' and ν_e were found by Rochester to have respectively the values of 814.5, 822.9, and 43935 cm.$^{-1}$ and are thus in good agreement with the predictions made above.*

TABLE VII

B–Cl AND B–Br DISTANCES AND FORCE CONSTANTS IN BCl,
BBr, BCl₃, AND BBr₃

—	in BX	in BX₃
r_0(B−Cl) $(10^{-8}$ cm.)	1.720	1.74 ⎫ X = Cl
k (B−Cl) $(10^5$ dynes/cm.)	3.391	3.30 ⎭
r_0(B−Br) $(10^{-8}$ cm.)	1.89	1.87 ⎫ X = Br
k (B−Br) $(10^5$ dynes/cm.)	2.612	2.50 ⎭

in the diatomic radical and the corresponding saturated molecule within the accuracy of the latter values. It may be mentioned that differences *greater* than ± 0.02Å in r_0 and $\pm 0.1 \cdot 10^5$ dynes/cm. in k are found when the C–H distances and force constants in free CH, in C_2H_2, CH_4, and C_2H_4 are compared while, on the other hand, the observed differences of the OH and SH distances and force constants in free OH and SH, and in H_2O and H_2S respectively are smaller than the limits given, as is the case for the boron halides. It is to be expected that with the more precise measurements for the four-atomic halides small differences of the same order as actually observed for OH–H_2O, SH–H_2S will be found.

Acknowledgment

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REACTION RATES OF THE OXIDATION OF LIQUID ACETALDEHYDE[1]

BY A. H. HEATLEY[2]

Abstract

In the commercial process for producing acetic anhydride and acid by the oxidation of acetaldehyde the observed concentrations of anhydride could not be accounted for till allowance was made for an important side reaction. The paper gives the differential equations based on the suggested mechanism; their solution is shown for certain limiting values of the reaction velocity coefficients, but in the general case numerical methods are required. Calculated and observed values are compared. Continuous operation of the process is also studied briefly.

Symbols Used

(Some symbols used only for a few times are not included)

a—$\frac{1}{2}(k_3 K_4)^{\frac{1}{2}}$,

$(\quad)_a$—An equation that is approximate, rather than exact,

k_1, k_2, k_4, k_6, k_7—Coefficients of reaction velocity,

k_3—Fraction of Reaction B that yields anhydride,

k_5—Coefficient of variation of k_4,

t—Time,

p, w, x, y, z—Concentrations of acetaldehyde, peracetic acid, acetic anhydride, water, and acetyl peroxide, respectively, as mole fractions,

A, B, C—Integration constants,

$D(x)$—$I_{1/3}(x)/I_{-1/3}(x)$,

$E(x)$—$I_{-2/3}(x)/I_{2/3}(x)$,

$I_n(x)$—Modified Bessel function of the first kind and the nth order,

$K_n(x)$—Modified Bessel function of the second kind and the nth order,

K_2, K_4, K_6, K_7—k_2/k_1, k_4/k_1, etc.,

K_{62}—$K_6/2K_2$,

$Q(x)$—$I_{2/3}(x)/I_{-1/3}(x)$,

R—Ratio of t to the total time required for the reaction,

S—Moles of acetaldehyde per mole of oxygen (input in continuous operation).

χ—$1/x$

θ—$1 + k_5 R$

κ—$(k_3 K_4)^{\frac{1}{2}}/3k_5$

μ—$K_2/8$
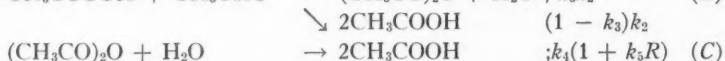
ρ—$1 - R$

ω—$w + \rho/2$

Introduction

A commercial process for producing acetic anhydride by the oxidation of acetaldehyde has been described by Benson (1). The concentrations of the anhydride present during the oxidation are of importance commercially, and an explanation of their variation was sought by the consideration of the consecutive and side reactions believed to occur.

Prior to the development of this process the oxidation of acetaldehyde was generally believed to follow the course:—

$$CH_3CHO + O_2 \rightarrow CH_3COOOH$$
$$CH_3COOOH + CH_3CHO \rightarrow 2CH_3COOH,$$
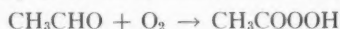
although it was recognized that there were intermediate stages in the reactions, at least under some conditions (2, 3, 4, 8, 10, and others). With the discovery of the formation of acetic anhydride a different set of equations was suggested:

$$CH_3CHO + O_2 \rightarrow CH_3COOOH \qquad\qquad ; k_1 \qquad (A)$$
$$CH_3COOOH + CH_3CHO \quad \rightarrow (CH_3CO)_2O + H_2O ; k_3k_2 \qquad (B)$$
$$\searrow 2CH_3COOH \qquad (1 - k_3)k_2$$
$$(CH_3CO)_2O + H_2O \qquad\quad \rightarrow 2CH_3COOH \qquad ;k_4(1 + k_5R) \quad (C)$$

In addition there may be side reactions:

$$(CH_3CO)_2O + CH_3COOOH \rightarrow (CH_3CO)_2O_2 + CH_3COOH ; k_6 \qquad (D)$$
$$(CH_3CO)_2O_2 + H_2O \qquad\quad \rightarrow CH_3COOOH + CH_3COOH ; k_7 \qquad (E)$$

The *problem* was to determine whether experimental data could be explained by the comparatively simple mechanism of Equations A, B, C, and, if not, whether the assumption of the side reactions D and E (for which there was some chemical evidence) could account for the observed trends of the anhydride concentration.

The *method*, briefly stated, was (*a*) to set up the system of differential equations corresponding to Equations A to E, (*b*) to calculate from these the values of anhydride concentration at various times (expressed as time ratio), using various assumed values of the rate constants, and (*c*) to compare these calculated values with those observed in experiments.

The complete solution of the system of differential equations was not achieved, but, for the data under consideration, certain approximations valid over a wide range lead to considerable simplification. The solutions* are given for several limiting cases because they may be of interest to those studying similar reactions, and because they assist in making preliminary estimates of the constants involved in the present work. The expressions for the concentrations of peracetic acid and of acetyl peroxide and a brief discussion of the continuous process are also given for the sake of completeness.

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* It must be emphasized that though these results involve mathematical functions rare in chemical work they should neither be feared nor respected more than the simple exponential function in the results for a reaction of the first order. These functions merely enable us to obtain the logical consequences of the assumptions involved in equations A to E in numerical form, so that they may be compared with experimental data.

The Differential Equations and Their Solution

The condition considered in these computations is the addition of oxygen to the system at a uniform rate which, owing to its instantaneous reaction with the acetaldehyde, determines the rate of formation of peracetic acid (k_1 mole fraction per hour). Let t be the time at any instant, and R the ratio of t to the total time required (at the constant rate specified) to add the oxygen equivalent to all the aldehyde; since this total time is obviously $1/2k_1$, $R = 2k_1t$. Let p, w, x, y, and z be the concentrations in mole fractions of acetaldehyde, peracetic acid, acetic anhydride, water, and acetyl peroxide, respectively; the concentration of acetic acid is then $1 - (p + w + x + y + z)$. The reaction velocity coefficients are shown to the right of the various reactions to which they apply; the fraction k_3 of Reaction B yields the anhydride, the fraction $1 - k_3$ yields the acid. Experiments undertaken without reference to the oxidation reaction have indicated that the velocity coefficient for reaction C increases* as the aldehyde decreases. It is assumed that the variation is linear with respect to R:—** Velocity coefficient for $C = k_4(1 + k_5R)$.

The concentration of the various substances then follows the equations below, derived from Equations A to E.

$$\frac{dp}{dt} = -k_1 - k_2pw, \tag{1}$$

$$\frac{dw}{dt} = k_1 - k_2pw - k_6wx + k_7yz, \tag{2}$$

$$\frac{dx}{dt} = k_3k_2pw - k_4(1 + k_5R)xy - k_6wx, \tag{3}$$

$$\frac{dy}{dt} = k_3k_2pw - k_4(1 + k_5R)xy - k_7yz, \tag{4}$$

$$\frac{dz}{dt} = k_6wx - k_7yz. \tag{5}$$

It is more convenient to work in terms of R, the time ratio, and for convenience we write K_2 for k_2/k_1, K_4 for k_4/k_1, etc. With these changes we have

$$2\frac{dp}{dR} = -1 - K_2pw, \tag{6}$$

$$2\frac{dw}{dR} = 1 - K_2pw - K_6wx + K_7yz, \tag{7}$$

$$2\frac{dx}{dR} = k_3K_2pw - K_4(1 + k_5R)xy - K_6wx, \tag{8}$$

$$2\frac{dy}{dR} = k_3K_2pw - K_4(1 + k_5R)xy - K_7yz, \tag{9}$$

$$2\frac{dz}{dR} = K_6wx - K_7yz. \tag{10}$$

* *Plyler and Barr have also noted a variation in this reaction coefficient (12).*
**See also Appendix C.*

By inspection we note that

$$dp - dw - dz = -dR; \quad p - w - z = 1 - R, \tag{11}$$

$$dx - dy + dz = 0; \quad y = x + z. \tag{12}$$

Evaluation of w and z

The further solution of these equations obviously is quite impractical until it is noted that certain approximations are available owing to our knowledge of some of the experimental results. The values of w and of z are very low, except perhaps as R approaches unity; therefore K_2 is large. Whence we may say:—

from Equation (11) $p \approx 1 - R$; then $dp/dR = -1$ (13)*$_a$

from Equation (6) $K_2pw = 1; \quad w = 1/K_2(1 - R).$ (14)**$_a$

Since z is small, $dz/dR \approx 0$, whence

from Equation (10) $K_6wx - K_7(x + z)z = 0,$ (15)$_a$

then $z \approx (K_6/K_7)w = K_6/K_2K_7(1 - R).$ (16)$_a$

A rough value of the error of these approximations may be obtained as follows. By definition, let

$$w = \frac{1 + \Delta w}{K_2(1 - R)} \text{ and } z = (1 + \Delta z)(K_6w/K_7). \tag{17}$$

From Equation (11)

$$p = 1 - R + (w + z) \approx 1 - R + w(1 + K_6/K_7). \tag{18}_a$$

From Equation (18)

$$\frac{dp}{dR} \approx -1 + (1 + K_6/K_7) \cdot \frac{1 + \Delta w}{K_2(1 - R)^2}. \tag{19}_a$$

From Equation (6)

$$\frac{dp}{dR} = -\tfrac{1}{2} - \frac{K_2}{2}wp = -\tfrac{1}{2} - \frac{1 + \Delta w}{2(1 - R)}\{1 - R + w(1 + K_6/K_7)\}. \tag{20}_a$$

Equating the right sides of Equations (19) and (20) and solving we have

$$\Delta w = \frac{-3(1 + K_6K_7)}{K_2(1 - R)^2 + 4(1 + K_6/K_7)}. \tag{21}_a$$

From Equation (10)

$$2\frac{dz}{dR} = K_6wx - K_7xz - K_7z^2. \tag{22}$$

From Equation (17)

$$2\frac{dz}{dR} \approx 2(1 + \Delta z)\frac{K_6}{K_7}\frac{(1 + \Delta w)}{K_2(1 - R)^2}. \tag{23}_a$$

Equating the right sides of these equations we have

$$\Delta z = -\frac{2K_2 + K_6}{2K_2 + 2K_6 + K_2K_7x(1 - R)}. \tag{24}_a$$

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*   * Equations involving an approximation will be designated by a subscript "a". The ≈ sign will be used only the first time a new approximation is introduced.*

*   ** When z is zero and K_2 = 8000, this approximation is about 0.15%, 0.24%, 0.41%, and 0.94% high at R = 0.5, 0.6, 0.7, and 0.8. respectively. When corrected by Equation (21) it is about 1% low at R = 0.94 and more accurate at all lower values of R. These data are based on Equation (32). When z is not zero but does not exceed w, a careful estimate indicates that Equation (14) is not more than 1.2% high at R = 0.8, so that we are justified in using this approximation up to R = 0.8, as we do later in this paper.*

The approximations for w and z given in Equations (14) and (16) even when modified by the corrections in Equations (17), (21), and (24) are obviously inapplicable when R is nearly zero or unity. However, *when K_6 is zero*, i.e., when no acetyl peroxide is formed, the exact value of w can be found. Equation (7) reduces to

$$2 \frac{dw}{dR} = 1 - K_2 pw. \tag{25}$$

Since z is zero, $p = w + 1 - R$. Now put

$$\rho = 1 - R \qquad \text{and} \qquad \omega = w + \rho/2. \tag{26}$$

Then

$$\frac{d\omega}{d\rho} - \frac{K_2}{2} \omega^2 = - \frac{K_2}{8} \rho^2. \tag{27}$$

The solution of this equation is given in Appendix A.

$$\omega = -f(\mu,\rho) \cdot \rho/2, \tag{28}$$

where

$$f(\mu,\rho) = \frac{I_{-3/4}(\mu\rho^2) - CI_{3/4}(\mu\rho^2)}{I_{1/4}(\mu\rho^2) - CI_{-1/4}(\mu\rho^2)}, \tag{29}$$

and $\mu = K_2/8$. Reverting to the original variable,

$$w = \omega - \rho/2 = \{- f(\mu,\rho) - 1\}\rho/2. \tag{30}$$

When $R = 0$ and $\rho = 1$, $w = 0$ and therefore $f(\mu,\rho) = -1$ whence

$$C = \frac{I_{1/4}(\mu) + I_{-3/4}(\mu)}{I_{3/4}(\mu) + I_{-1/4}(\mu)}. \tag{31}$$

For convenience of form we write

$$w = \{U(\mu,\rho) - 1\}\rho/2, \tag{32}$$

where

$$U = \frac{I_{-3/4}(\mu\rho^2) - CI_{3/4}(\mu\rho^2)}{CI_{-1/4}(\mu\rho^2) - I_{1/4}(\mu\rho^2)}.$$

As $R \to 1$, $\rho \to 0$, the I functions of positive order become zero, and

$$w \text{ (at } R = 1) = \frac{\rho}{2}\left\{ \frac{(-\frac{1}{4})!}{\rho C(-\frac{3}{4})!}\left(\frac{2}{\mu}\right)^{\!3} - 1 \right\} = \frac{0.6760}{CK_2^{\frac{3}{4}}}. \tag{33}$$

Evaluation of x

To proceed to the evaluation of x, we insert the approximate values of p, w, and y from Equations (12) to (14) in Equation (8) and obtain

$$2 \frac{dx}{dR} = k_3 - K_4 (1 + k_5R)x^2 - \frac{K_6}{K_2(1 - R)} x. \tag{34}_a$$

A solution of this equation has not been obtained, except for particular cases.

When k_5 is zero, put $\rho = 1 - R$, then $d\rho = -dR$. Write K_{62} for $K_6/2K_2$.

$$\frac{dx}{d\rho} = - \frac{k_3}{2} + K_{62} \cdot \frac{x}{\rho} + \frac{K_4}{2} x^2. \tag{35}_a$$

Now put

$$x = - \frac{K_{62} + 1}{K_4\rho} - \frac{2}{K_4 t} \frac{dt}{d\rho}. \tag{36}_a$$

Then

$$\frac{dx}{d\rho} = \frac{K_{62} + 1}{K_4\rho^2} - \frac{2}{K_4 t} \frac{d^2t}{d\rho^2} + \frac{2}{K_4 t^2}\left(\frac{dt}{d\rho}\right)^{\!2}. \tag{37}_a$$

Equating the right sides of Equations (35) and (37) we have

$$\frac{d^2t}{d\rho^2} + \frac{1}{\rho}\frac{dt}{d\rho} - \left\{ \frac{k_3 K_4}{4} + \left(\frac{K_{62}+1}{2}\right)^2 \cdot \frac{1}{\rho^2} \right\} t = 0. \tag{38}_a$$

This is the well known Bessel equation whose solution is

$$t = A I_n(a\rho) + B K_n(a\rho) \quad (n \text{ is an integer}), \tag{39}_a$$

$$t = A I_n(a\rho) + B I_{-n}(a\rho) \quad (n \text{ is not an integer}), \tag{40}_a$$

where $n = \frac{1}{2}(K_{62}+1)$ and $a = \frac{1}{2}(k_3 K_4)^{\frac{1}{2}}$. Reverting to the original variable

$$x = \frac{2a}{K_4} \cdot \frac{C K_{n-1}(a\rho) - I_{n-1}(a\rho)}{C K_n(a\rho) + I_n(a\rho)} \quad (n \text{ integral}) \tag{41}_a$$

Since $y = 0$ when $\rho = 1$, $C = I_{n-1}(a)/K_{n-1}(a)$. Alternatively

$$x = \frac{2a}{K_4} \cdot \frac{- I_{n-1}(a\rho) + C' I_{-n+1}(a\rho)}{I_n(a\rho) - C' I_{-n}(a\rho)} \quad (n \text{ not integral}). \tag{42}_a$$

Since $y = 0$ when $\rho = 1$, $C' = I_{n-1}(a)/I_{-n+1}(a)$.
When $K_6 = 2K_2$, $K_{62} = 1$, $n = 1$, and

$$x = \frac{2a}{K_4} \cdot \frac{C K_0(a\rho) - I_0(a\rho)}{C K_1(a\rho) + I_1(a\rho)}, \tag{43}_a$$

where $C = I_0(a)/K_0(a)$. When $K_6 = K_2$, $K_{62} = \frac{1}{2}$, $n = \frac{3}{4}$ and

$$x = \frac{2a}{K_4} \cdot \frac{C' I_{1/4}(a\rho) - I_{-1/4}(a\rho)}{I_{3/4}(a\rho) - C' I_{-3/4}(a\rho)}, \tag{44}_a$$

where $C' = I_{-1/4}(a)/I_{1/4}(a)$. When $K_6 = \frac{2}{3} K_2$, $n = \frac{2}{3}$ and

$$x = \frac{2a}{K_4} \cdot \frac{I_{1/3}(a\rho) - D(a)I_{-1/3}(a\rho)}{D(a)I_{2/3}(a\rho) - I_{-2/3}(a\rho)}, \tag{45}_a$$

where $D(a) = I_{1/3}(a)/I_{-1/3}(a)$. When $K_6 = 0$, $n = \frac{1}{2}$ and

$$x = \frac{2a}{K_4} \cdot \frac{C'' I_{\frac{1}{2}}(a\rho) - I_{-\frac{1}{2}}(a\rho)}{I_{\frac{1}{2}}(a\rho) - C'' I_{-\frac{1}{2}}(a\rho)}, \tag{46}_a$$

where $C'' = I_{-\frac{1}{2}}(a)/I_{\frac{1}{2}}(a)$. Since $I_{\frac{1}{2}}(a\rho)/I_{-\frac{1}{2}}(a\rho) = \tanh a\rho = \tanh(a - aR)$

$$x = \frac{2a}{K_4} \tanh aR \tag{47}_a$$

In order to ascertain the effects of various changes in the coefficients upon the results, we now consider the case in which k_2 *is infinite* and k_6 *is zero*. w and z become zero, p becomes exactly $1 - R$ and the differential equation for x collapses to

$$2\frac{dx}{dR} = k_3 - K_4(1 + k_5 R)x^2. \tag{48}$$

To get this equation in workable form we put

$$\theta = 1 + k_5 R \quad \text{and} \quad \chi = 1/x. \tag{49}$$

Then we have the Riccati equation

$$\frac{d\chi}{d\theta} + \frac{k_3}{2k_5}\chi^2 = \frac{K_4}{2k_5}\theta. \tag{50}$$

This corresponds to Equation (1) in Appendix A and the solution is given there in Equation (11), the corresponding symbols being χ, u; θ, x; $k_3/2k_5$, b; $K_4/2k_5$, c; 1, m. We write at once

$$x = \frac{1}{\chi} = \left(\frac{k_3}{K_4\theta}\right)^{\frac{1}{2}} \cdot \frac{I_{1/3}(\kappa\theta^{3/2}) - D(\kappa)I_{-1/3}(\kappa\theta^{3/2})}{I_{-2/3}(\kappa\theta^{3/2}) - D(\kappa)I_{2/3}(\kappa\theta^{3/2})}, \tag{51}$$

where $D(\kappa) = I_{1/3}(\kappa)/I_{-1/3}(\kappa)$ and $\kappa = (k_3K_4)^{\frac{1}{2}}/3k_5$.

When k_5 is zero, Equation (48) becomes

$$2\frac{dx}{dR} = k_3 - K_4x^2, \tag{52}$$

whence

$$x = (2a/K_4) \tanh aR, \tag{53}$$

If Equation (52) is integrated between the limits x_1 and x_2, R_1 and R_2, instead of between zero and x or R, we have

$$x_2 = \frac{x_1 + (2a/K_4)\tanh a\Delta R}{1 + x_1(K_4/2a)\tanh a\Delta R}. \tag{54}*$$

Note that Equation (53) is the same as the approximate equation (47). For the former, K_2 is large; for the latter, K_2 is infinite. Likewise Equation (51) gives an approximate value of x when K_2 is large but not infinite (and K_6 is zero).

For convenience of reference Table I indicates the various combinations of restrictions on the constants that have been studied and gives the number of the important equations that correspond.

TABLE I

EQUATIONS CORRESPONDING TO VARIOUS RESTRICTIONS ON THE CONSTANTS

K_2	k_5	K_6	Equation numbers
Large	N.r.	N.r.	13, 14, 16, 21, 24, 34
Large	N.r.	0	32, 33
Large	0	$2K_2$	43
Large	0	K_2	44
Large	0	$2K_2/3$	45, 71
Large	0	0	47
∞	N.r.	0	51, 72
∞	0	0	53, 54

NOTE 1. *N.r. means no restrictions.*
NOTE 2. *There are no restrictions on k_3, K_4. K_7 has no meaning when K_6 is zero.*

Continuous Operation

This reaction is carried out as a continuous process by adding acetaldehyde and oxygen at a uniform rate and withdrawing an equivalent amount of the reaction liquid, which is kept homogeneous by mixing. The calculations below refer to the steady state. It is assumed that the input of acetaldehyde

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* *Theoretically, the integration of other equations in this paper could also be done between limits neither of which is zero; practically, it is impossible owing to the complicated form of the constants of integration.*

is S moles per mole of oxygen, and, since the fraction $(1 - p)$ of acetaldehyde reacts with the oxygen and the peracetic acid and the balance, p, flows out unchanged with the effluent, its net input is $S(1 - p)$ moles per mole of oxygen. Similarly a correction term is added to the equations for the other constituents. The variation factor for k_5 is also changed to be (approximately) equal to $(1 - p)$ as before.   Then

$$\frac{dp}{dt} = -k_1 - k_2pw + Sk_1 - pSk_1 = 0, \tag{55}$$

$$\frac{dw}{dt} = +k_1 - k_2pw - k_6wx + k_7yz - wSk_1 = 0, \tag{56}$$

$$\frac{dx}{dt} = k_3k_2pw - k_4\{1 + 2k_5/S\}xy - k_6wx - xSk_1 = 0, \tag{57}$$

$$\frac{dy}{dt} = k_3k_2pw - k_4\{1 + 2k_5/S\}xy - k_7yz - ySk_1 = 0, \tag{58}$$

$$\frac{dz}{dt} = k_6wx - k_7yz - zSk_1 = 0. \tag{59}$$

From Equations (55), (56), and (59)

$$dp - dw - dz = -2k_1 + Sk_1\{1 - (p - w - z)\} = 0 \tag{60}$$

$$\therefore S = \frac{2}{1 - (p - w - z)}, \tag{61}$$

$$p \approx (S - 2)/S \tag{62}_a$$

From Equations (57), (58), and (59)

$$dx - dy + dz = Sk_1(x - y + z) = 0, \tag{63}$$

$$\therefore x - y + z = 0; \qquad y = x + z. \tag{64}$$

From Equations (55) and (62)

$$K_2pw = S - pS - 1 \approx 1, \tag{65}_a$$

$$p = \frac{S - 1}{K_2w + S}. \tag{66}$$

Solving Equations (62) and (66)

$$w = \frac{S}{K_2(S - 2)}. \tag{67}_a$$

From Equation (59)

$$z = \frac{K_6wx}{K_7y + S} \approx \frac{K_6}{K_7}w. \tag{68}_a$$

From Equations (57), (65), and (67)

$$k_3 - K_4\left(1 + \frac{2k_5}{S}\right)x^2 - \frac{K_6Sx}{K_2(S-2)} - Sx = 0. \tag{69}_a$$

Then

$$x = \frac{-b + (b^2 + 4rk_3)^{\frac{1}{2}}}{2r}, \tag{70}_a$$

where

$$b = \frac{K_6S}{K_2(S - 2)} - S; \quad r = \frac{K_4(S + 2K_5)}{S}.$$

A higher yield of anhydride is obtained if an inert diluent is continuously added with the acetaldehyde (1), and calculations like the above have been made for this case. However, since they involve the rather bold assumption that the various reaction coefficients are the same as before, the results are not given.

Computation of Data

Most of the data to be computed require the use of functions not well known. Tables of tanh x (Equations (47), (53), and (54)) are available in many chemical handbooks and in books of mathematical tables. Excellent tables of quarter-integral (Equations (32) and (44)) and third-integral (Equations (45) and (51)) Bessel functions I are now being computed (14). No quarter-integral I tables are now available and the only tables of third-integral I functions (9, p. 285) cannot be used for interpolation, so that modification of the equations is necessary. Equation (45) is rewritten in the form—

$$x = \frac{2a}{K_4} \cdot \frac{\{1 - D(a\rho)\} - \{1 - D(a)\}}{Q(a\rho)[\{E(a\rho) - 1\} + \{1 - D(a)\}]} \,, \tag{71}_a$$

and Equation (51) is given the form

$$x = \left(\frac{k_3}{K_4\theta}\right)^{\frac{1}{4}} \cdot \frac{\{1 - D(\kappa)\} - \{1 - D(\kappa\theta^{3/2})\}}{Q(\kappa\theta^{3/2}) [\{1 - D(\kappa)\} + \{E(\kappa\theta^{3/2}) - 1\}]} \,, \tag{72}$$

where

$$D(x) = I_{1/3}(x)/I_{-1/3}(x), \quad Q(x) = I_{2/3}(x)/I_{-1/3}(x)$$

and

$$E(x) = I_{-2/3}(x)/I_{2/3}(x).$$

Tables of the functions $Q(x)$, $1 - D(x)$, and $E(x) - 1$ are given in Table II; the methods of computation are given in Appendix B. Tables of the Bessel functions I and K of the zero and first orders (Equation (43)) are available (13, Table II, pages 698–713) and (5). They are interpolable.

Several methods are available for the numerical evaluation of x from Equation (34), no solution of which could be found. For the data given below, Ford's method was used (6). Since the last term of Equation (34) is an approximation that becomes too inaccurate for reliable results when R exceeds 0.8 (for the value of constants used in these calculations), further values could be obtained only by reverting to the set of Equations (6) to (10), a very laborious task that has not been undertaken.

Owing to the increase of weight, the relation between the mole fraction and the percentage by weight varies during the reaction. The molecular weight at the beginning is 44 (acetaldehyde); the average molecular weight at the end, i.e., when $R = 1$, is 60. Whence we have the relation

$$\text{Percentage by weight} = \frac{\text{mole fraction} \times \text{molecular weight}}{44 + 16R} \times 100\%$$

For continuous operation, the denominator of the above expression becomes $44 + 32/S$.

TABLE II

VALUES OF FUNCTIONS USED IN EQUATIONS (71) AND (72)

x	$Q(x)$	$1 - D(x)$	$\dfrac{\log}{1 - D(x)}$	$\Delta \log$	$E(x) - 1$	$\dfrac{\log}{E(x) - 1}$	$\Delta \log$
0.0	0.0000	1.000	0.0000	−1703	∞	—	—
.2	.1486	6.756×10^{-1}	$\bar{1}.8297$	1340	6.4367	0.8087	−4751
.4	.2897	4.963	.6957	1368	2.1557	.3336	3188
.6	.4169	3.621	.5589	1428	1.0346	.0148	2586
.8	.5267	2.607	.4161	1488	5.704×10^{-1}	$\bar{1}.7562$	2278
1.0	0.6182	1.850	$\bar{1}.2673$	1542	3.376	$\bar{1}.5284$	2101
.2	.6920	1.297	.1131	1586	2.081	.3183	1989
.4	.7505	9.005×10^{-2}	$\bar{2}.9545$	1621	1.317	.1194	1917
.6	.7961	6.200	.7924	1647	8.47×10^{-2}	$\bar{2}.9277$	1874
.8	.8315	4.243	.6277	1667	5.50	.7403	1834
2.0	0.8587	2.891	$\bar{2}.4610$	1684	3.605	$\bar{2}.5569$	1811
.2	.8799	1.962	.2926	1694	2.376	.3758	1795
.4	.8963	1.328	.1232	1704	1.571	.1963	1783
.6	.9091	8.970×10^{-3}	$\bar{3}.9528$	1710	1.042	.0180	1773
.8	.9192	6.050	.7818	1715	6.929×10^{-3}	$\bar{3}.8407$	1767
3.0	0.9274	4.077	$\bar{3}.6103$	1720	4.613	$\bar{3}.6640$	1762
.2	.9341	2.744	.4383	1721	3.075	.4878	1758
.4	.9395	1.846	.2662	1725	2.051	.3120	1755
.6	.9442	1.241	.0937	1726	1.369	.1365	1752
.8	.9481	8.339×10^{-4}	$\bar{4}.9211$	1727	9.148×10^{-4}	$\bar{4}.9613$	1751
4.0	0.9514	5.603	$\bar{4}.7484$	1729	6.113	$\bar{4}.7862$	1748
.2	.9543	3.763	.5755	1729	4.087	.6114	1748
.4	.9569	2.527	.4026	1731	2.733	.4366	1746
.6	.9591	1.696	.2295	1731	1.828	.2620	1746
.8	.9612	1.139	.0564	1732	1.223	.0874	1745
5.0	0.9629	7.642×10^{-5}	$\bar{5}.8832$	1731	8.183×10^{-5}	$\bar{5}.9129$	1744
.2	.9646	5.130	.7101		5.476	.7385	
.4	.9660						
.6	.9675						
.8	.9686						
6.0	0.9698						
.4	.9718						
.8	.9737						
7.2	.9753						
.6	.9767						
8.0	.9779						

Calculated and Observed Data

In the case of reactions of low order as usually studied one determines the reaction coefficients by relatively simple calculations direct from the experimental data. In the present case this method is limited to the determination of k_1, known from the oxygen input, and k_6, k_7 known roughly from the concentration of the corresponding chemicals, which the analytical methods do not sharply distinguish. For the remaining k's the only available method is to reproduce the experimental graph of x *versus* R by a suitable combination of k's and K's. Some economy of effort is achieved by first using Equation

(53), the simplest of all, to obtain a rough idea of some of the constants, and then proceeding to drop the simplifying assumptions.

Fig. 1 shows the experimental data for the concentration of anhydride, x, *versus* the time ratio, R, for several runs, using various conditions, and those calculated by means of several equations, the values of the constants being selected to give the closest possible approach to the general form of the observed curves, but no attempt being made to duplicate closely any of them. It is obvious that only Curve 4 or minor modifications of it can duplicate the observed data; thus the constants used in making that curve are the required reaction coefficients; a reaction mechanism excluding the side reactions (D) and (E) would be inadequate.

Curve	Equation	K_2	k_3	K_4	k_5	K_6
1	53	∞	0.64	64	0	0
2	51, 72	∞	0.81	44	1	0
3	45, 71	8000	0.44	20	0	5333
4	34	8000	0.64	25	1	8000
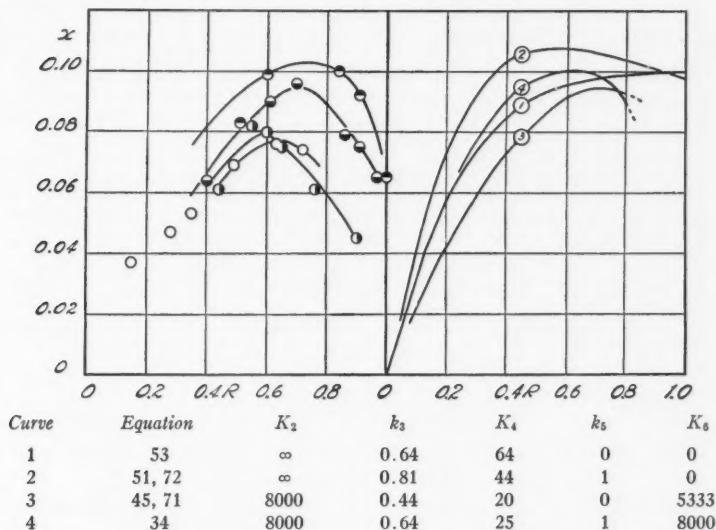
FIG. 1. *Acetic anhydride mole fraction, x, vs. time ratio, R. Left, observed; right, calculated.*

It should be noted that the reaction proposed by Bowen and Tietz (4) as the source of acetyl peroxide, namely

$$CH_3COOOH + CH_3COOH \rightarrow (CH_3CO)_2O_2 + H_2O \qquad (F)$$
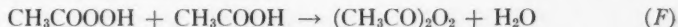
is highly improbable, for if it replaces reaction (D) in the mechanism, there is no K_6 in the differential equation for x; and it has just been seen that the experimental graph for x cannot be duplicated without assigning a substantial value to K_6.

The data for continuous operation using the reaction coefficients of Curve 4 above are given in Table III, as well as the corresponding data for batch operation. These show clearly that the advantages of the continuous process are offset by a greatly decreased yield of x, acetic anhydride, the more valuable

product.   In practice this disadvantage is reduced by the use of an inert diluent (1).

TABLE III

VALUES OF x FOR VARIOUS TIME RATIOS (BATCH) AND INPUT RATIOS (CONTINUOUS)

R	x	S	x
0.0	0.000	2.4	0.058
.2	.058	2.8	.069
.4	.091	3.2	.072
.5	.098	3.6	.073
.6	.100	4.0	.073
.7	.099	4.8	.071
.8	.089		

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This problem was suggested by Mr. G. Benson, Assistant Director of the Plant Research Department, to whom grateful acknowledgment is made for helpful discussion of much of the material presented.

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Appendix A

THE SOLUTION OF THE RICCATI EQUATION

Cf. Equations (27) and (50)

In the Riccati Equation

$$\frac{du}{dx} + bu^2 = cx^m, \tag{1}$$

put

$$u = \frac{1}{bv} \cdot \frac{dv}{dx}. \tag{2}$$

Then

$$\frac{d^2v}{dx^2} - bcvx^m = 0. \tag{3}$$

Now put

$$w = \frac{2}{m+2} x^{\frac{m+2}{2}}. \tag{4}$$

Then

$$\frac{d^2v}{dw^2} + \frac{m}{m+2} \cdot \frac{dv}{wdw} - bcv = 0. \tag{5}$$

Next put

$$v = rw^{\frac{1}{m+2}}. \tag{6}$$

Then

$$\frac{d^2r}{dw^2} + \frac{1}{w} \cdot \frac{dr}{dw} - \left\{ bc + \left(\frac{1}{m+2}\right)^2 \frac{1}{w^2} \right\} r = 0, \tag{7}$$

which is the well known Bessel Equation. If bc is positive the solution is

$$r = AI_p(w\sqrt{bc}) + BI_{-p}(w\sqrt{bc}) \tag{8a}$$

when $p = 1/(m+2)$ is not an integer or zero; or

$$r = AI_p(w\sqrt{bc}) + BK_p(w\sqrt{bc}) \tag{8b}$$

when p is an integer or zero. I_p and K_p are modified Bessel* functions of the first and second kind respectively. Reverting to the variables v and x, and taking the case when p is not integral or zero,

$$v = x^{\frac{1}{2}}\{AI_p(gx^{\frac{1}{2p}}) + BI_{-p}(gx^{\frac{1}{2p}}) \tag{9}$$

$$\frac{dv}{dx} = (bc)^{\frac{1}{2}}x^{\frac{m+1}{2}}\{AI_{p-1}(gx^{\frac{1}{2p}}) + BI_{-p+1}(gx^{\frac{1}{2p}}), \tag{10}$$

where $g = 2p(bc)^{\frac{1}{2}} = 2(bc)^{\frac{1}{2}}/(m+2)$. Then from Equation (2)

$$u = \frac{(bc)^{\frac{1}{2}}}{b} x^{\frac{m}{2}} \frac{I_{p-1}(gx^{\frac{1}{2p}}) + CI_{-p+1}(gx^{\frac{1}{2p}})}{I_p(gx^{\frac{1}{2p}}) + CI_{-p}(gx^{\frac{1}{2p}})}. \tag{11a}$$

The corresponding equation when p is an integer or zero is

$$u = \frac{(bc)^{\frac{1}{2}}}{b} x^{\frac{m}{2}} \frac{I_{p-1}(gx^{\frac{1}{2p}}) - CK_{p-1}(gx^{\frac{1}{2p}})}{I_p(gx^{\frac{1}{2p}}) + CK_p(gx^{\frac{1}{2p}})}. \tag{11b}$$

The constant C is to be determined from the boundary or initial conditions applying to the differential equation.

The above development follows that given by Forsyth (7, pp. 195, 196) who, however, proceeds only as far as the equivalent of the writer's Equation (8).

Appendix B
COMPUTATION OF TABLE II, PAGE 270.

From $x = 0$ to 8.0, $Q(x)$ was computed from the tabulated values of $I_{2/3}(x)$ and $I_{-1/3}(x)$. For higher values of x the difference between $I_{1/3}(x)$ and $I_{-1/3}(x)$ is negligible and $Q(x)$ may be computed from the approximate formula

$$Q(x) \approx \frac{1 - \dfrac{7}{72x} - \dfrac{7}{72x} \cdot \dfrac{65}{144x} - \dfrac{7}{72x} \cdot \dfrac{65}{144x} \cdot \dfrac{209}{216x} - \ \cdot\ \cdot\ \cdot\ \cdot}{1 + \dfrac{5}{72x} + \dfrac{5}{72x} \cdot \dfrac{77}{144x} + \dfrac{5}{72x} \cdot \dfrac{77}{144x} \cdot \dfrac{221}{216x} + \ \cdot\ \cdot\ \cdot\ \cdot},$$

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* *Bessel functions of various kinds are much used by physicists and electrical engineers, but as far as the author is aware, they have not hitherto appeared in chemical problems.*

which is derived from the asymptotic formulae for the I functions. For values of $x > 10$ this may be replaced by

$$Q(x) \approx 1 - \frac{1}{6x} - \frac{5}{72x^2},$$

with an error not exceeding 1 in 5000.

Because the functions $1 - D(x)$ and $E(x) - 1$ are not suitable for interpolation, their logarithms and logarithmic differences are tabulated. The computation of the former was based on the right-hand expression in

$$1 - D(x) = \frac{I_{-1/3}(x) - I_{1/3}(x)}{I_{-1/3}(x)} = \frac{(\sqrt{3}/\pi)e^x K_{1/3}(x)}{e^x I_{-1/3}(x)}.$$

The values of $e^x K_{1/3}(x)$ were taken from Watson (13, Table III, pages 714–29). Since there is no published table of $K_{2/3}(x)$, the same method cannot be used for $E(x) - 1$. From $x = 0$ to 1.8, $E(x)$ was computed as indicated by its definition Equation (72) page 269, and then log $\{E(x) - 1\}$ was taken from tables. From $x = 2.0$ to 5.2, the computation was made in the same way using tables to nine significant figures kindly supplied in advance of publication by Dr. A. N. Lowan (14). Apart from these entries, the table is believed to be reliable to only 1 part in 1000 owing to unreliable final digits in the Jahnke-Emde table (9, p. 285). Several erronous values in their table were recomputed.

Appendix C

The result given below is not used in the present paper but is so closely related that it is desirable to record it here.

If the reaction velocity coefficient of reaction C is a linear function of x instead of R, Equation (48) becomes

$$2\frac{dx}{dR} = k_3 - K_4(1 + k_8 x)x^2 = k_3 - K_4 x^2 - K_4 k_8 x^3. \tag{C1}$$

The maximum value of x is now found by equating the right side of Equation (C1) to zero, using the actual numerical values of the various constants. Let h be this maximum value of x. Then

$$\frac{dx}{dR} = \frac{k_3}{2h}(h - x)\left(1 + \frac{x}{h} + \frac{K_4 k_8 h x^2}{k_3}\right). \tag{C2}$$

Rearranging and integrating, we have

$$R = \frac{2h}{k_3} \int_o^x \frac{dx}{(h - x)f(x)}, \tag{C3}$$

where $f(x) = 1 + x/h + K_4 k_8 h x^2/k_3$. The value of this integral may be taken from Peirce's table (11). Inserting the values at the two limits we have

$$R = \frac{h}{2k_3 + h^3 K_4 k_8}\left\{ 2.3026 \log \frac{f(x)}{(1 - x/h)^2} + \right.$$

$$\frac{2}{\sqrt{q}}(2K_4 k_8 h^2/k_3 + 1/h)\left(\tan^{-1}\frac{2K_4 k_8 h x/k_3 + 1/h}{\sqrt{q}} - \tan^{-1}\frac{1}{h\sqrt{q}}\right)\right\}, \tag{C4}$$

where $q = 4K_4 k_8 h/k_3 - 1/h^2$.

CONTRIBUTION TO THE STUDY OF *CIS-TRANS* ISOMERS DERIVED FROM 3,3-DIPHENYL-1-HYDRINDONE. SYNTHESIS OF 3,3-DIPHENYLHYDRINDENE AND SOME OF ITS DERIVATIVES[1]

BY PAUL E. GAGNON[2] AND LS. PHIL. CHARETTE[3]

Abstract

Cis-trans isomers were obtained by condensation of 3,3-diphenyl-1-hydrindone with benzaldehyde or its *o*- and *m*-methyl-, *o*- and *p*-methoxy-, *o*-ethoxy, *o*- and *p*-chloro-derivatives, and by conversion of the condensation products by treatment with acetic acid.

3,3-Diphenyl-1-hydrindone was reduced to 3,3-diphenylhydrindene, and the condensation products of that ketone with the above mentioned aldehydes to derivatives of 3,3-diphenylhydrindene.

The methods of preparation of *trans*- and *cis*-3,3-diphenyl-2-benzylidene-1-hydrindone and of 3,3-diphenylhydrindene have been improved and the following compounds are described, as far as the authors are aware, for the first time: *trans*- and *cis*-3,3-diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone, *trans*- and *cis*-3,3-diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone, *trans*- and *cis*-3,3-diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone, *trans*- and *cis*-3,3-diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone, *trans*- and *cis*-3,3-diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone, *trans*- and *cis*-3,3-diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone, *trans*- and *cis*-3,3-diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone, 3,3-diphenyl-2-benzyl-hydrindene, 3,3-diphenyl-2-(*o*-methylbenzyl)-hydrindene, 3,3-diphenyl-2-(*m*-methylbenzyl)-hydrindene, 3,3-diphenyl-2-(*o*-methoxybenzyl)-hydrindene, 3,3-diphenyl-2-(*p*-methoxybenzyl)-hydrindene, 3,3-diphenyl-2-(*o*-ethoxybenzyl)-hydrindene, 3,3-diphenyl-2-(*o*-chlorobenzyl)-hydrindene, 3,3-diphenyl-2-(*p*-chlorobenzyl)-hydrindene.

Introduction

In previous work, one of the present authors (7) succeeded in isolating the two isomeric forms of 3,3-diphenyl-2-benzylidene-1-hydrindone (III), (IV), by condensation of 3,3-diphenyl-1-hydrindone (I) with benzaldehyde. The same author (7) prepared 3,3-diphenyl-hydrindene (II) from 3,3-diphenyl-1-hydrindone by Wolff's method (14), which consists in heating the hydrazone or the semicarbazone of the carbonyl compound with sodium ethoxide to about 170 to 180° C.
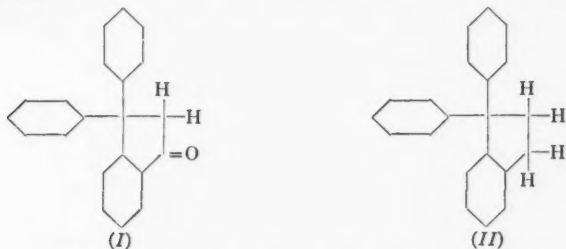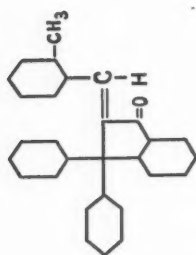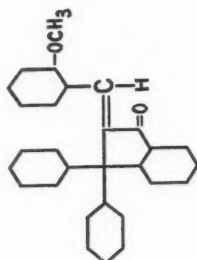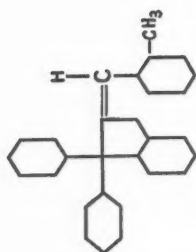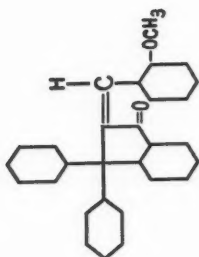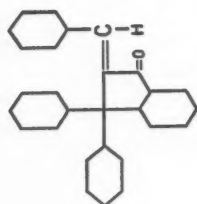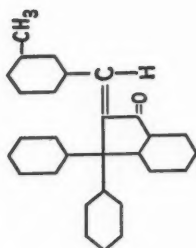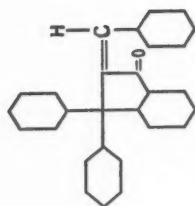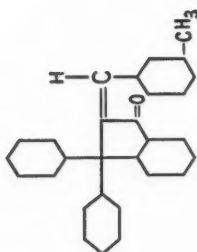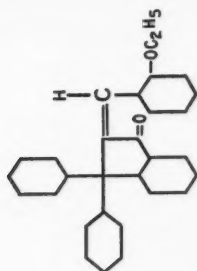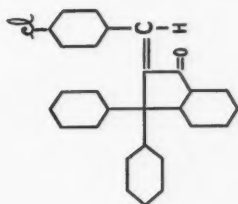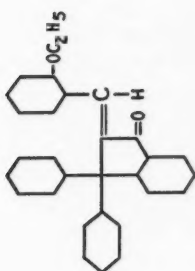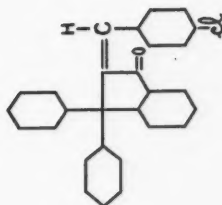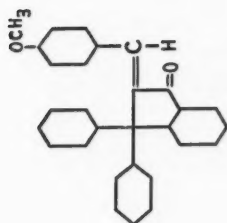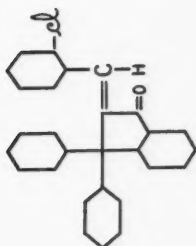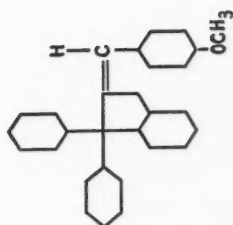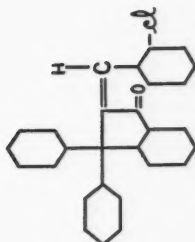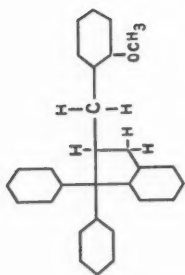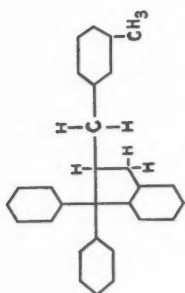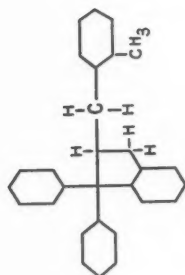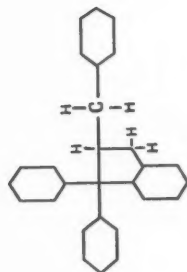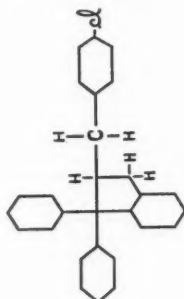
(I)   (II)

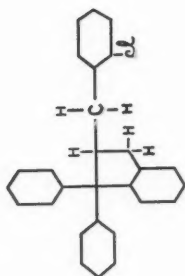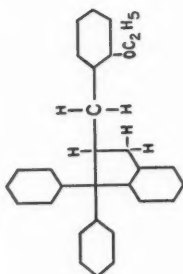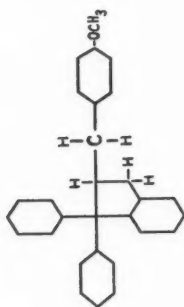The main object of the present work was to obtain, by condensation of 3,3-diphenyl-1-hydrindone with benzaldehyde and its derivatives, the isomeric compounds predicted by theory and to reduce them to 3,3-diphenylhydrindene derivatives.

The method used by Gagnon (7) for the condensation of 3,3-diphenyl-1-hydrindone with benzaldehyde consisted in adding, at room temperature, alcoholic potash to a solution of the ketone in benzaldehyde. The mixture was left standing and, two days later, a mixture of crystals of different colour was obtained. By very slow evaporation of a benzene solution of this mixture and sorting by hand, the two isomers were separated, one canary-yellow melting at 192° C. and the other pale yellow melting at 172° C.

The same compounds were prepared in this work by a slightly different method. The ketone and benzaldehyde were dissolved in boiling methyl alcohol and alcoholic potash was added. After about three hours of subsequent boiling, not a mixture, but only one canary-yellow compound melting at 192° C., which is the *trans*-form of 3,3-diphenyl-2-benzylidene-1-hydrindone (III), was obtained. By means of boiling glacial acetic acid it was converted into its isomer melting at 172° C. (IV).

By condensing, in the presence of alcoholic potash, 3,3-diphenyl-1-hydrindone with benzaldehyde derivatives and treating the condensation products with glacial acetic acid, similar results were obtained, except in the case of *o*-ethoxybenzaldehyde where the reaction product was almost only the *cis*-form. In this way were obtained:

the canary-yellow *trans*-3,3-diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone melting at 190° C. (V) and its white *cis*-isomer melting at 176° C. (VI);

the nearly white *trans*-3,3-diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone melting at 175° C. (VII) and its canary-yellow *cis*-isomer melting at 104° C. (VIII);

the white *trans*-3,3-diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone melting at 216° C. (IX) and its canary-yellow *cis*-isomer melting at 182° C. (X);

the nearly white *trans*-3,3-diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone melting at 163° C. (XI) and its canary-yellow *cis*-isomer melting at 133° C. (XII);

the canary-yellow *cis*-3,3-diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone melting at 153° C. (XIII) and its darker *trans*-isomer melting at 161° C. (XIV);

the canary-yellow *trans*-3,3-diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone melting at 197° C. (XV) and its white *cis*-isomer melting at 151° C. (XVI);

the pale yellow *trans*-3,3-diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone melting at 201° C. (XVII) and its canary-yellow *cis*-isomer melting at 176° C. (XVIII).

It is generally known that there is a surprising regularity in the differences in physical properties between the *cis*- and *trans*-forms. The *cis*-form usually

has the lower melting point, the greater solubility in inert solvents, and is the labile form. This enables us to distinguish the *cis*-forms from the *trans*-forms (Table I).

TABLE I

SOLUBILITY OF *cis-trans* ISOMERS IN 100 ML. OF 95% ETHYL ALCOHOL AT 78.5° C.

Isomers	M.p., °C.*	Solubility, gm.
trans-3,3-Diphenyl-2-benzylidene-1-hydrindone	192	0.5
cis-3,3-Diphenyl-2-benzylidene-1-hydrindone	172	1.5
trans-3,3-Diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone	190	0.5
cis-3,3-Diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone	176	2.0
trans-3,3-Diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone	175	0.9
cis-3,3-Diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone	104	2.5
trans-3,3-Diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone	216	0.4
cis-3,3-Diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone	182	0.6
trans-3,3-Diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone	163	1.0
cis-3,3-Diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone	133	1.7
trans-3,3-Diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone	161	1.2
cis-3,3-Diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone	153	1.4
trans-3,3-Diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone	197	0.5
cis-3,3-Diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone	151	3.0
trans-3,3-Diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone	201	0.5
cis-3,3-Diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone	176	1.0

* *The melting points are uncorrected.*

As previously stated, by condensing 3,3-diphenyl-1-hydrindone with benzaldehyde or its derivatives, in each experiment as reaction product only one isomer was obtained except in the case of *o*-ethoxybenzaldehyde, which will be discussed later in this paper. The other isomer was obtained by treatment with acetic acid. Since the latter isomer is more soluble and melts at the lower temperature, it was named the *cis*-form and the former, the *trans*-form.

Moreover, it was observed that the *trans*-form was really the stable one. In fact, when 3,3-diphenyl-1-hydrindone was condensed with benzaldehyde or its *o*- and *m*-methyl-, *o*- and *p*-methoxy-, *o*- and *p*-chloro-derivatives, only the *trans*-form melting at the higher temperature was obtained. On boiling this *trans*-form in glacial acetic acid and by fractional crystallization the *cis*-form was obtained. The product from the first crystallization was not the pure *cis*-form, but a mixture of the two forms: the melting point of this mixture was intermediate between those of the *trans*- and *cis*-forms. The pure *cis*-form was obtained only after the second crystallization. Apparently an equilibrium is established during the conversion. On heating the *trans*-form at a temperature a little higher than its melting point, a mixture of the two isomers was obtained. On the other hand, on boiling the *cis*-form in methyl

alcohol in the presence of potash, it was completely converted into its *trans*-isomer. According to these observations, the *trans*-form melting at the higher temperature is the stable one.

In the condensation of 3,3-diphenyl-1-hydrindone with *o*-ethoxybenzaldehyde, the *cis*-form melting at 153° C. was the first to be obtained. The filtrate was then left standing for several hours. The *trans*-form, melting at 161° C., crystallized. The ratio of the *cis*- to the *trans*-form was 11 to 2. On boiling the *cis*-form in glacial acetic acid, it was completely converted into its *trans*-isomer. The same result was obtained when heating the *cis*-form to about 165° C. for a few seconds. This explains the fact that the melting point of the mixture of the two isomers is 161° C., the same as that of the *trans*-form. Here also the *cis*-form melting at the lower temperature is the labile one. The two isomers have virtually the same melting points; this is in agreement with the fact that they have nearly the same solubility and colour.

It was intended to apply the reduction method of Wolff to the condensation products, as Gagnon (7) did in the case of 3,3-diphenyl-1-hydrindone. However, on account of the decrease of reactivity of the CO group caused by replacement of the hydrogen atoms of the neighbouring CH_2 group by a benzylidene group, it was impossible to obtain the hydrazones of the condensation products by the method used for the preparation of the hydrazone of 3,3-diphenyl-1-hydrindone (7, 10). The authors then tried Clemmensen's method (3, 4, 5), which enabled them to obtain directly, from the carbonyl compounds, 3,3-diphenylhydrindene and the following derivatives:

3,3-diphenyl-2-benzylhydrindene (XIX),

3,3-diphenyl-2-(*o*-methylbenzyl)-hydrindene (XX),

3,3-diphenyl-2-(*m*-methylbenzyl)-hydrindene (XXI),

3,3-diphenyl-2-(*o*-methoxybenzyl)-hydrindene (XXII),

3,3-diphenyl-2-(*p*-methoxybenzyl)-hydrindene (XXIII),

3,3-diphenyl-2-(*o*-ethoxybenzyl)-hydrindene (XXIV),

3,3-diphenyl-2-(*o*-chlorobenzyl)-hydrindene (XXV),

3,3-diphenyl-2-(*p*-chlorobenzyl)-hydrindene (XXVI).

This paper is divided into two parts. In the first, the condensation products of 3,3-diphenyl-1-hydrindone with benzaldehyde or its derivatives, and also the isomers of these condensation products are described. The second part deals with 3,3-diphenylhydrindene and some of its derivatives.

As all the condensation products and their isomers were prepared by the same general method, the preparation of the first will be described in detail. Only the quantities of materials and any differences in experimental conditions and procedure will be given in the case of the others. The same applies to the derivatives of 3,3-diphenyl-1-hydrindene.

PART I

3,3-Diphenyl-1-hydrindone (I)

According to the methods of Fosse (6) and Hellerman (8), triphenylcarbinol (2400 gm.) was condensed with malonic acid (1560 gm.) in the presence of acetic anhydride (960 ml.) and, by elimination of water and carbon dioxide, triphenylpropionic acid was obtained.   Yield, 2700 gm. (96.8%).

Several methods of preparation of 3,3-diphenyl-1-hydrindone by cyclization of triphenylpropionic acid are described.   The process used by Moureu, Dufraisse, and Dean (9) and improved by Gagnon (7) eliminates a molecule of water from triphenylpropionic acid by means of concentrated sulphuric acid.   Bergmann and Weiss (2) obtain the ketone by elimination of hydrochloric acid from triphenylpropionyl chloride.   Unger (13) treated triphenylpropionic acid with monochloracetic anhydride.   He pointed out that the melting point of 3,3-diphenyl-1-hydrindone was 121° C.   By the method of Moureu, Dufraisse, and Dean, a large quantity of 3,3-diphenyl-1-hydrindone melting at 131° C. and not at 121° C., as stated by Unger, was prepared. The results obtained are in agreement with the data of the previously mentioned authors, except Unger, and also with those of Auwers and Hügel (1), who prepared this ketone by a different method, by cyclization of β-chloro-*trans*-cinnamyl chloride.

3,3-Diphenyl-2-benzylidene-1-hydrindones (7), (III), (IV)

By condensing 3,3-diphenyl-1-hydrindone with benzaldehyde, *trans*-3,3-diphenyl-2-benzylidene-1-hydrindone melting at 192° C. was obtained.   This ketone was then converted into its *cis*-isomer melting at 172° C.

(a) Preparation of Isomer Melting at 192° C. (III)

In a round bottomed flask (1000 ml.) fitted with a reflux condenser, 3,3-diphenyl-1-hydrindone (15 gm.) and benzaldehyde (10 ml.) were dissolved in boiling absolute methyl alcohol (300 ml.).   The mixture was kept boiling and, through the condenser, 100 ml. of alcoholic potash (300 gm. of potassium hydroxide in 1000 ml. of absolute methyl alcohol) was slowly added.   After three and a half hours of subsequent boiling, the mixture was allowed to cool, and it was then filtered.   The yellow crystalline product, washed with water and ethyl alcohol, was crystallized from benzene; m.p. 192° C.   The compound separated from ethyl alcohol in hexagonal prisms.   Yield, 15.7 gm. (80%).   This canary-yellow compound was identified as 3,3-diphenyl-2-benzylidene-1-hydrindone (7) by a mixed melting point determination. Soluble in hot glacial acetic acid, it is almost insoluble in methyl and ethyl alcohols.

(b) Preparation of Isomer Melting at 172° C. (IV)

A concentrated solution of *trans*-3,3-diphenyl-2-benzylidene-1-hydrindone in glacial acetic acid was boiled for 14 hr. and then left standing at room

temperature.   After several hours, a mixture of products melting at 167 to 187° C. was separated.   From the filtrate another product, pale yellow and more soluble, crystallized.   After recrystallization from benzene this product melted at 172° C.   The compound separated from alcohol in pyramid-shaped crystals.   It was identified as 3,3-diphenyl-2-benzylidene-1-hydrindone (7) by a mixed melting point determination.   On boiling a methyl alcohol solution of this compound in presence of potash, its *trans*-isomer was obtained.

3,3-Diphenyl-2-(o-methylbenzylidene)-1-hydrindones (V), (VI)

By condensing 3,3-diphenyl-1-hydrindone with *o*-tolualdehyde, *trans*-3,3-diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone melting at 190° C. was obtained.   This ketone was then converted into its *cis*-isomer melting at 176° C.

(a) Preparation of Isomer Melting at 190° C. (V)

3,3-Diphenyl-1-hydrindone (10 gm.), *o*-tolualdehyde (7 ml.), absolute methyl alcohol (200 ml.), alcoholic potash (70 ml.); boiling time, 4 hr.

The canary-yellow product, washed with water and ethyl alcohol, was crystallized from glacial acetic acid; m.p. 189° C.   Yield, 12 gm. (87.6%). Recrystallized from ethyl alcohol, in which it is very slightly soluble, this compound melts at 190° C.   It separated from ethyl alcohol in needle-shaped crystals.   It is soluble in hot benzene, very slightly soluble in methyl alcohol, but insoluble in ether and petroleum ether.   Calc. for $C_{29}H_{22}O$: C, 90.16; H, 5.7%.   Found: C, 89.42; H, 5.78%.

(b) Preparation of Isomer Melting at 176° C. (VI)

trans-3,3-Diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone treated in the manner described above yielded a yellow product melting at 163 to 186° C. From the filtrate, another product crystallized.   It was recrystallized, perfectly white, from ethyl alcohol; m.p. 176° C.   The compound separated from ethyl alcohol in needle-shaped crystals (cluster of needles).   This compound is more soluble in the usual solvents than its isomer melting at 190° C. Calc. for $C_{29}H_{22}O$: C, 90.16; H, 5.70%.   Found: C, 88.9; H, 5.8%.

3,3-Diphenyl-2-(m-methylbenzylidene)-1-hydrindones (VII), (VIII)

By condensing 3,3-diphenyl-1-hydrindone with *m*-tolualdehyde, *trans*-3,3-diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone melting at 175° C. was obtained.   This ketone was then converted into its *cis*-isomer melting at 104° C.

(a) Preparation of Isomer Melting at 175° C. (VII)

3,3-Diphenyl-1-hydrindone (15 gm.), *m*-tolualdehyde (10 ml.), methyl alcohol (300 ml.), alcoholic potash (100 ml.); boiling time, 2 hr.

The pale yellow product, washed with water and ethyl alcohol, was crystallized from glacial acetic acid; m.p. 172° C.   Yield, 16.5 gm. (81%).   Recrystallized from ethyl alcohol, in which it is very slightly soluble, it melts at 175° C.   The compound separated from ethyl alcohol in elongated prisms. It is white, and is soluble in hot benzene, and very slightly soluble in methyl

alcohol and ether.   Calc. for $C_{29}H_{22}O$: C, 90.16; H, 5.70%.   Found: C, 89.60; H, 5.79%.

(b) Preparation of Isomer Melting at 104° C. (VIII)

trans-3,3-Diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone treated in the usual manner yielded a yellow product melting at 157 to 172° C.   From the filtrate, another canary-yellow product crystallized.   It was recrystallized twice from ethyl alcohol; m.p. 104° C.   The compound separated from ethyl alcohol in small hexagonal prisms.   This compound is more soluble in the usual solvents than its isomer melting at 175° C.   Calc. for $C_{29}H_{22}O$: C, 90.16; H, 5.70%.   Found: C, 89.50; H, 5.78%.

3,3-Diphenyl-2-(o-methoxybenzylidene)-1-hydrindones (IX), (X)

By condensing 3-3-diphenyl-1-hydrindone with *o*-methoxybenzaldehyde, *trans*-3,3-diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone melting at 216° C. was obtained.   This ketone was then converted into its *cis*-isomer melting at 182° C.

(a) Preparation of Isomer Melting at 216° C. (IX)

3,3-Diphenyl-1-hydrindone (12 gm.), *o*-methoxybenzaldehyde (6 ml.), absolute methyl alcohol (240 ml.), alcoholic potash (80 ml.); boiling time, 3 hr.

The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from benzene; m.p. 216° C.   It separated from ethyl alcohol in small elongated prisms.   Yield, 12 gm. (90%).   This compound is soluble in hot glacial acetic acid, but almost insoluble in methyl and ethyl alcohols, ether, and petroleum ether.   Calc. for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47%.   Found: C, 86.35; H, 5.53%.

(b) Preparation of Isomer Melting at 182° C. (X)

trans-3,3-Diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone yielded a yellow product melting at 168 to 214° C.   From the filtrate, another canary-yellow product crystallized.   It was recrystallized from ethyl alcohol; m.p. 182° C.   The compound separated from ethyl alcohol in needle-shaped crystals.   It is more soluble in the usual solvents than its isomer melting at 175° C.   Calc. for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47%.   Found: C, 83.6; H, 5.5%.

3,3-Diphenyl-2-(p-methoxybenzylidene)-1-hydrindones (XI), (XII)

By condensing 3,3-diphenyl-1-hydrindone with *p*-methoxybenzaldehyde, *trans*-3,3-diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone melting at 162° C. was obtained.   This ketone was then converted into its *cis*-isomer melting at 133° C.

(a) Preparation of Isomer Melting at 163° C. (XI)

3,3-Diphenyl-1-hydrindone (20 gm.), *p*-methoxybenzaldehyde (10 ml.), absolute methyl alcohol (400 ml.), alcoholic potash (140 ml.).

After three hours of boiling, the reflux condenser was replaced by another condenser, the alcohol distilled off, and the residue dissolved in benzene. The solution was washed with water, dried over anhydrous sodium sulphate, and completely evaporated. On cooling, a red solid product was obtained which, after several washings with ether and crystallizations from glacial acetic acid and ethyl alcohol, became almost white; m.p. 163° C. The compound separated from ethyl alcohol in elongated prisms. Yield, 5 gm. (17.7%). It is soluble in hot benzene, and slightly soluble in methyl and ethyl alcohols. Calc. for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47%. Found: C, 86.46; H, 5.41%.

(b) Preparation of Isomer Melting at 133° C. (XII)

trans-3,3-Diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone yielded a yellow product melting at 150 to 161°. From the filtrate, another canary-yellow product crystallized. It was recrystallized from ethyl alcohol; m.p. 133° C. The compound separated from ethyl alcohol in rectangular prisms. It is more soluble in the usual solvents than its isomer melting at 163° C. Calc. for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47%. Found: C, 84.7; H, 5.5%.

3,3-Diphenyl-2-(o-ethoxybenzylidene)-1-hydrindones (XIII), (XIV)

By condensing 3,3-diphenyl-1-hydrindone with *o*-ethoxybenzaldehyde, *cis*-3,3-diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone melting at 153° C. was obtained. This ketone was then converted into its *trans*-isomer melting at 161° C.

(a) Preparation of Isomer Melting at 153° C. (XIII)

3,3-Diphenyl-1-hydrindone (10 ml.), *o*-ethoxybenzaldehyde (6 ml.), absolute methyl alcohol (200 ml.), alcoholic potash (70 ml.); boiling time, 5 hr.; flask, 500 cc.

The canary-yellow product, washed with water and ethyl alcohol, was crystallized from glacial acetic acid; m.p. 153° C. Yield, 12.2 gm. From the original filtrate, another dark yellow product crystallized; m.p. 161° C. The mixed melting point was 161° C. Total yield, 13.7 gm. (94%). Soluble in cold benzene, the compound melting at 153° C. is but slightly soluble in methyl and ethyl alcohols, ether, and petroleum ether. It separated from ethyl alcohol in elongated prisms. Calc. for $C_{30}H_{24}O_2$: C, 86.54; H, 5.77%. Found: C, 86.03; H, 5.85%.

(b) Preparation of Isomer Melting at 161° C. (XIV)

cis-3,3-Diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone in glacial acetic acid was treated in the usual manner. After a few hours, the solution was filtered and the dark yellow product crystallized from ethyl alcohol; m.p. 161° C. By heating the *cis*-isomer melting at 153° C. to about 165° C. for a few seconds it was converted into the other form melting at 161° C. This compound melting at 161° C. is darker than its *cis*-isomer, but has about the same solubility in the usual solvents. The compound separated from ethyl alcohol in elongated prisms. Calc. for $C_{30}H_{24}O_2$: C, 86.54; H, 5.77%. Found: C, 85.72; H, 5.80%.

3,3-Diphenyl-2-(o-chlorobenzylidene)-1-hydrindones (XV), (XVI)

By condensing 3-3-diphenyl-1-hydrindone with *o*-chlorobenzaldehyde, *trans*-3,3-diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone melting at 197° C. was obtained. This ketone was then converted into its *cis*-isomer melting at 151° C.

(a) Preparation of Isomer Melting at 197° C. (XV)

3,3-Diphenyl-1-hydrindone (15 gm.), *o*-chlorobenzaldehyde (7 ml.), absolute methyl alcohol (300 ml.), alcoholic potash (100 ml.); boiling time, 3 hr.

The canary-yellow product, washed with water and ethyl alcohol, was crystallized from benzene; m.p. 197° C. The compound separated from ethyl alcohol in needle-shaped crystals. Yield, 20 gm. (90%). It is soluble in hot glacial acetic acid, but almost insoluble in methyl and ethyl alcohols, ether, and petroleum ether. Calc. for $C_{28}H_{19}OCl$: Cl, 8.73%. Found: Cl, 8.81%.

(b) Preparation of Isomer Melting at 151° C. (XVI)

trans-3,3-Diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone yielded a yellow product melting at 170 to 195° C. By diluting the filtrate with water, another product was precipitated. It was crystallized, perfectly white, from ethyl alcohol; m.p. 151° C. The compound separated from ethyl alcohol in hexagonal prisms. It is more soluble in the usual solvents than its isomer melting at 197° C. Calc. for $C_{28}H_{19}OCl$: Cl, 8.73%. Found: Cl, 8.72%.

3,3-Diphenyl-2-(p-chlorobenzylidene)-1-hydrindones (XVII), (XVIII)

By condensing 3,3-diphenyl-1-hydrindone with *p*-chlorobenzaldehyde, *trans*-3,3-diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone melting at 201° C. was obtained. This ketone was then converted into its *cis*-isomer melting at 176° C.

(a) Preparation of Isomer Melting at 201° C. (XVII)

3,3-Diphenyl-1-hydrindone (10 gm.), *p*-chlorobenzaldehyde (6 gm.), absolute methyl alcohol (200 ml.), alcoholic potash (70 ml.); boiling time, 3 hr.; flask, 500 cc.

The pale yellow product, washed with water and ethyl alcohol, was crystallized from glacial acetic acid; m.p. 201° C. The compound separated from ethyl alcohol in irregular prisms. Yield, 13 gm. (91%). This compound, soluble in cold benzene, is almost insoluble in methyl and ethyl alcohols, ether, and petroleum ether. Calc. for $C_{28}H_{19}OCl$: Cl, 8.73%. Found: Cl, 8.92%.

(b) Preparation of Isomer Melting at 176° C. (XVIII)

From *trans*-3,3-diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone a yellow product melting at 180 to 197° C. was obtained. From the filtrate, another canary-yellow product crystallized. It was recrystallized from ethyl alcohol; m.p. 176° C. The compound separated from ethyl alcohol in elongated prisms. It is more soluble in the usual solvents than its isomer melting at 201° C. Calc. for $C_{28}H_{19}OCl$: Cl, 8.73%. Found: Cl, 8.74%.

PART II

3,3-DIPHENYLHYDRINDENE AND ITS DERIVATIVES

The reduction of 3,3-diphenyl-1-hydrindone and its condensation products with aldehydes was carried out by Clemmensen's method (3, 4, 5).

3,3-Diphenylhydrindene (II)

The amalgamated zinc was prepared in a round bottomed flask (500 ml.) by covering granulated zinc (50 gm.) with a 5% aqueous solution of mercuric chloride (100 ml.). After standing for one hour, the solution was poured off and 3,3-diphenyl-1-hydrindone (5 gm.), dissolved in glacial acetic acid (125 ml.), was added to the amalgamated zinc. The mixture was brought to boiling and, drop by drop, concentrated hydrochloric acid (150 ml.) was added. After one hour, the mixture was allowed to cool. The upper oily layer, which consisted of 3,3-diphenylhydrindene, was removed from the reaction mixture by dissolving in petroleum ether. The ether solution was washed with sodium bicarbonate solution and water and dried over anhydrous sodium sulphate. The ether was distilled off and the residue taken up with methyl alcohol and decolorized with charcoal. The alcohol was evaporated, whereupon a white product crystallized. Yield, 4 gm. (84%). Recrystallized from methyl alcohol, it melts at 67° C. It was identified as 3,3-diphenylhydrindene (7) by a mixed melting point determination.

3,3-Diphenyl-2-benzylhydrindene (XIX)

Into a round bottomed flask (500 ml.) fitted with a reflux condenser and containing amalgamated zinc (50 gm.), was poured a solution of *trans*-3,3-diphenyl-2-benzylidene-1-hydrindone (2.5 gm.) in glacial acetic acid (100 ml.). The mixture was brought to boiling and, drop by drop, concentrated hydrochloric acid (100 ml.) was added. A light coloured crystalline product formed on the surface. After one hour, the mixture was allowed to cool, and it was then filtered. This reduction process was repeated twice. The final product was recrystallized, perfectly white, from glacial acetic acid; m.p. 179° C. Yield, 1.7 gm. (70%). It is soluble in hot benzene, but is almost insoluble in methyl and ethyl alcohols, ether, and petroleum ether. Calc. for $C_{28}H_{24}$: C, 93.33; H, 6.67%. Found: C, 92.1; H, 6.6%.

3,3-Diphenyl-2-benzylhydrindene (XIX)

cis-3,3-Diphenyl-2-benzylidene-1-hydrindone (3.5 gm.), glacial acetic acid (100 ml.), amalgamated zinc (50 gm.), concentrated hydrochloric acid (100 ml.); flask, 1000 ml.

A light-coloured crystalline product formed on the surface. After one hour, the mixture was allowed to cool, and it was then filtered. The reduction was complete. The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from benzene; m.p. 179° C. Yield, 2.5 gm. (74%). It was identified as 3,3-diphenyl-2-benzylhydrindene by a mixed melting point determination. The *cis*-isomer was reduced much more easily and quickly than

the *trans*. Paal and Schiedewitz (11, 12) made the same observations when reducing some *cis-* and *trans*-acids.

3,3-Diphenyl-2-(o-methylbenzyl)-hydrindene (XX)

trans-3,3-Diphenyl-2-(*o*-methylbenzylidene)-1-hydrindone (6 gm.), glacial acetic acid (200 ml.), amalgamated zinc (50 gm.), concentrated hydrochloric acid (150 ml.); flask, 1000 ml.

A light-coloured crystalline product formed on the surface. After one hour and a half, the mixture was allowed to cool, and it was then filtered. The purification of the product required four crystallizations from glacial acetic acid; m.p. 132° C. Yield, 4 gm. (69%). The compound is white, is soluble in cold benzene and ether, but is almost insoluble in methyl and ethyl alcohols. Calc. for $C_{29}H_{26}$: C, 93.05; H, 6.95%. Found: C, 92.49; H, 6.93%.

3,3-Diphenyl-2-(m-methylbenzyl)-hydrindene (XXI)

trans-3,3-Diphenyl-2-(*m*-methylbenzylidene)-1-hydrindone (5 gm.), glacial acetic acid (200 ml.), amalgamated zinc (50 gm.), concentrated hydrochloric acid (150 ml.); flask, 1000 ml.

A light-coloured crystalline product formed on the surface. After one hour and a half, the mixture was allowed to cool, and it was then filtered. The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from glacial acetic acid; m.p. 149° C. Yield, 4.2 gm. (78%). It is soluble in cold benzene and ether, but is almost insoluble in hot methyl and ethyl alcohols and petroleum ether. Calc. for $C_{29}H_{26}$: C, 93.05; H, 6.95%. Found: C, 92.0; 6.9%.

3,3-Diphenyl-2-(o-methoxybenzyl)-hydrindene (XXII)

trans-3,3-Diphenyl-2-(*o*-methoxybenzylidene)-1-hydrindone (3 gm.), glacial acetic acid (125 ml.), amalgamated zinc (25 gm.), concentrated hydrochloric acid (125 ml.).

A white crystalline product formed almost immediately. After 30 min., the mixture was allowed to cool, and it was then filtered. The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from glacial acetic acid; m.p. 176° C. Yield, 2.6 gm. (90%). The compound is soluble in hot benzene, but is insoluble in methyl and ethyl alcohols, ether and petroleum ether. Calc. for $C_{29}H_{26}O$: C, 89.23; H, 6.67%. Found: C, 88.75; H, 6.65%.

3,3-Diphenyl-2-(p-methoxybenzyl)-hydrindene (XXIII)

trans-3,3-Diphenyl-2-(*p*-methoxybenzylidene)-1-hydrindone (5 gm.), glacial acetic acid (200 ml.), amalgamated zinc (25 gm.), concentrated hydrochloric acid (150 ml.); flask, 1000 ml.

A white crystalline product formed rapidly on the surface. After one hour, the mixture was allowed to cool, and it was then filtered. The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from glacial acetic acid; m.p. 178° C. Yield, 4.1 gm. (85%). Soluble in hot benzene, this compound is insoluble in methyl and ethyl alcohols, ether, and petroleum ether. Calc. for $C_{29}H_{26}O$: C, 89.23; H, 6.67%. Found: C, 88.0; H, 6.6%.

3,3-Diphenyl-2-(o-ethoxybenzyl)-hydrindene (XXIV)

cis-3,3-Diphenyl-2-(*o*-ethoxybenzylidene)-1-hydrindone (5 gm.), glacial acetic acid (125 ml.), amalgamated zinc (25 gm.), concentrated hydrochloric acid (150 ml.).

A white crystalline product formed immediately on the surface. After 30 min. the mixture was allowed to cool, and it was then filtered. The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from glacial acetic acid; m.p. 170° C. Yield, 4.4 gm. (90%). It is soluble in cold benzene, but insoluble in methyl and ethyl alcohol, ether, and petroleum ether. Calc. for $C_{30}H_{23}O$: C, 89.10; H, 6.93%. Found: C, 88.53; H, 6.91%.

3,3-Diphenyl-2-(o-chlorobenzyl)-hydrindene (XXV)

trans-3,3-Diphenyl-2-(*o*-chlorobenzylidene)-1-hydrindone (6 gm.), glacial acetic acid (210 ml.), amalgamated zinc (50 gm.), concentrated hydrochloric acid (200 ml.); flask, 1000 cc.

A crystalline product formed on the surface. After one hour and a half, the mixture was allowed to cool, and it was then filtered. The product, washed with water and ethyl alcohol, was crystallized, perfectly white, from glacial acetic acid; m.p. 160° C. Yield, 4.7 gm. (80%). Soluble in cold benzene and ether, this compound is insoluble in methyl and ethyl alcohols and petroleum ether. Calc. for $C_{28}H_{23}Cl$: Cl, 8.99%. Found: Cl, 9.08%.

3,3-Diphenyl-2-(p-chlorobenzyl)-hydrindene (XXVI)

trans-3,3-Diphenyl-2-(*p*-chlorobenzylidene)-1-hydrindone (5 gm.), glacial acetic acid (200 ml.), amalgamated zinc (50 gm.), concentrated hydrochloric acid (100 ml.).

A white product formed rapidly on the surface. After one hour, the mixture was allowed to cool, and it was then filtered. The purification of the product required three crystallizations from glacial acetic acid; m.p. 156° C. Yield, 4 gm. (82.5%). It is white, and is soluble in cold benzene and ether, and slightly soluble in methyl and ethyl alcohols. Calc. for $C_{28}H_{23}Cl$: Cl, 8.99%. Found: Cl, 9.07%.

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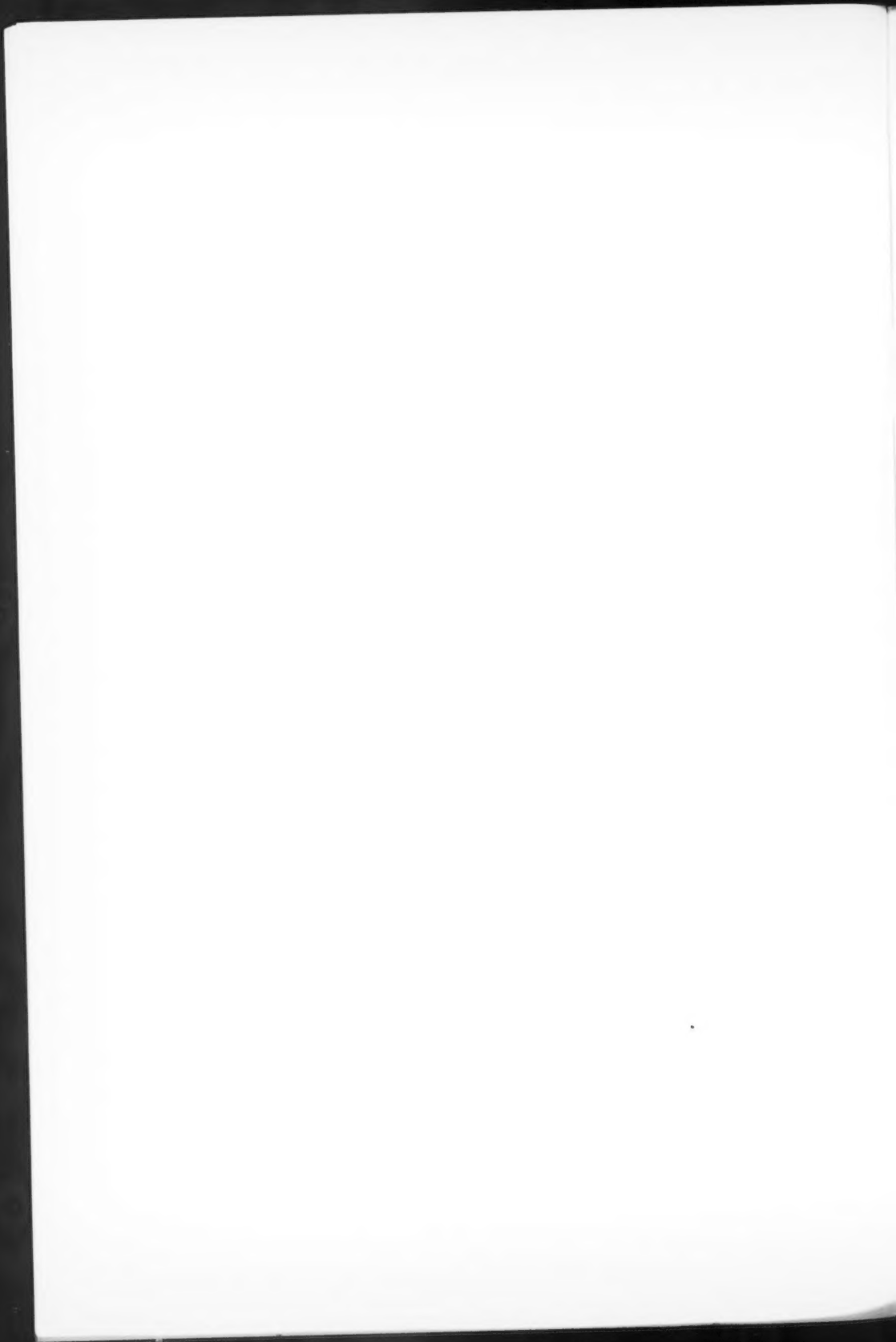
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